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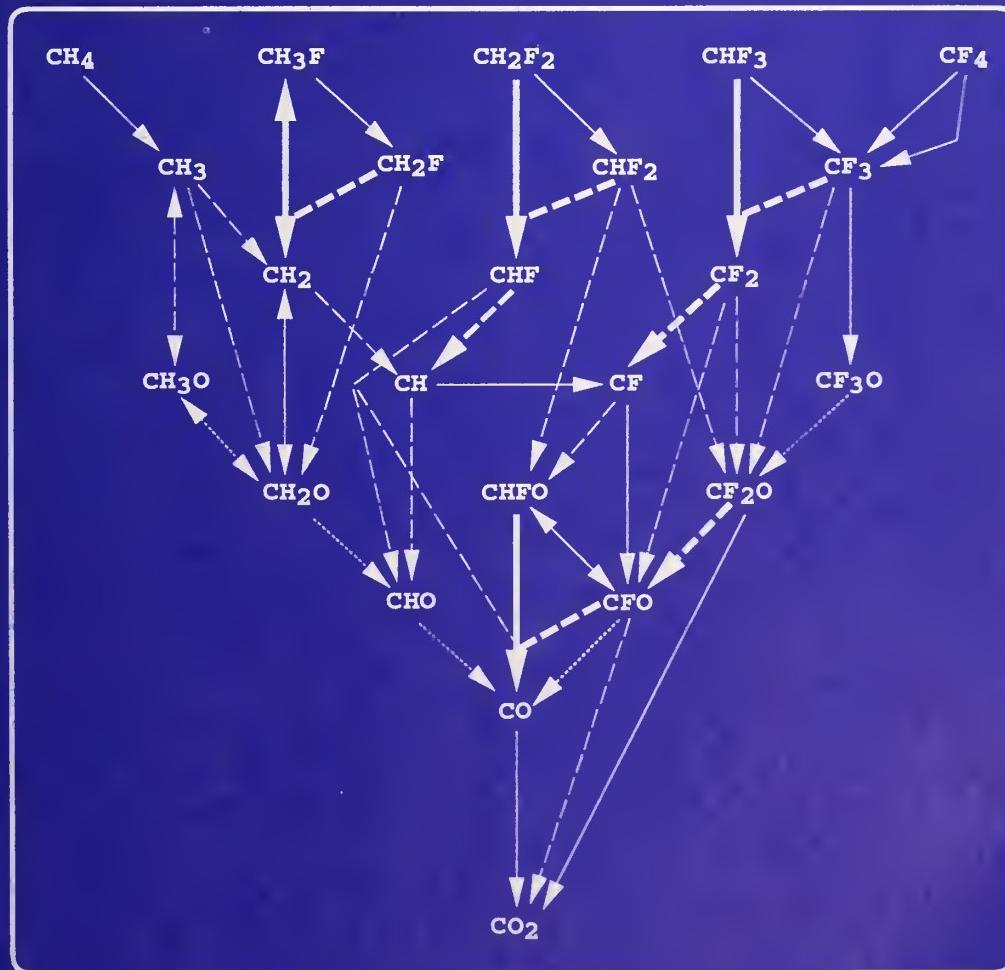
**NIST**

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**NIST Technical Note 1412**

***Thermochemical and Chemical Kinetic Data  
for Fluorinated Hydrocarbons***

**D. R. F. Burgess, Jr., M. R. Zachariah, W. Tsang, and P. R. Westmoreland**



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## EXECUTIVE SUMMARY

A comprehensive, detailed chemical kinetic mechanism was developed and is presented for C<sub>1</sub> and C<sub>2</sub> fluorinated hydrocarbon destruction and flame suppression. Existing fluorinated hydrocarbon thermochemistry and kinetics were compiled from the literature and evaluated. For species where no or incomplete thermochemistry was available, these data were calculated through application of *ab initio* molecular orbital theory. Group additivity values were determined consistent with experimental and *ab initio* data. For reactions where no or limited kinetics was available, these data were estimated by analogy to hydrocarbon reactions, by using empirical relationships from other fluorinated hydrocarbon reactions, by *ab initio* transition state calculations, and by application of RRKM and QRRK methods. The chemistry was modeled considering different transport conditions (plug flow, premixed flame, opposed flow diffusion flame) and using different fuels (methane, ethylene), equivalence ratios, agents (fluoromethanes, fluoroethanes) and agent concentrations. This report provides a compilation and analysis of the thermochemical and chemical kinetic data used in this work.



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# 1. Introduction

## 1.1. Overview

The thermochemical and chemical kinetic data presented here were compiled as a part of flame-inhibition modeling that was part of a large, short-term, intensive effort at NIST that evaluated (for the U.S. Air Force, Navy, Army and Federal Aviation Administration) potential fluorinated hydrocarbons and other agents as replacements for Halon 1301 ( $\text{CF}_3\text{Br}$ ). The modeling effort complemented the many experimental measurements in the overall NIST program, which characterized the effectiveness of various potential replacements. Our work focused on agent chemistry. This report is to provide documentation of the thermochemical and chemical kinetic data used in the modeling work. Further details of the evaluation of the thermochemical and chemical kinetic data and the *ab initio* calculations will be provided elsewhere, as will the results of the simulations of flame inhibition.

Halon 1301 is very effective as a chemical extinguisher. However, it is also extremely effective for depleting stratospheric ozone. Consequently, its production and use are restricted. The major objective of the modeling part of the overall work was to provide a chemical basis for rationalizing the relative degree of effectiveness of each candidate agent. A fundamental understanding of the chemistry of these agents in hydrocarbon flames should facilitate identification of desired characteristics of effective agents. That is, utilization of simple chemical concepts should enable screening and selection of potential agents with minimal time and human resources.

In order to accomplish this goal, it was necessary to develop a chemical mechanism based on elementary reaction steps for their destruction, their participation in and influence on hydrocarbon flame chemistry, as well as for prediction of potential by-products of incomplete combustion. However, neither a comprehensive mechanism nor a general review of the relevant the relevant chemistry existed prior to this study. Consequently, a significant effort was required in order simply to construct such a comprehensive mechanism prior to its use in any simulations. Further refinement of the mechanism requires experimental validation by flame measurements.

The focus of the mechanism development work was restricted to the chemistry involving only fluoromethanes and fluoroethanes. This includes both four of the candidate agents specifically being considered as replacements (i.e., CH<sub>2</sub>F<sub>2</sub>, CF<sub>3</sub>-CH<sub>2</sub>F, CF<sub>3</sub>-CHF<sub>2</sub>, CF<sub>3</sub>-CF<sub>3</sub>), as well as all of the other possible fluoromethanes and fluoroethanes. Larger fluorinated hydrocarbon agents (e.g., C<sub>3</sub>F<sub>8</sub>) and chlorine-substituted agents (e.g., CHF<sub>2</sub>Cl) were not explicitly considered in our study, because these additions significantly increase the complexity of the chemistry that must be considered. However, the effectiveness of each can be estimated to some degree by analogy to the other agents that were studied. This can be done by using the qualitative trends observed and the fundamental understanding of the chemistry developed by this and future work.

The complete set of fluoromethanes and fluoroethanes were studied for two basic reasons. These are discussed below.

First, when the four specific candidate agents being considered decompose in the flame, they generate a pool of fluorinated hydrocarbon stable species and radicals, which results in the formation of many of the other fluoromethanes and fluoroethanes. Consequently, in order to describe the decomposition of the four specific agents (and resultant chemistry) adequately, it is necessary to describe the chemistry of all of the many intermediates and products that are created, including most of the other fluoromethanes and fluoroethanes. For example, the lowest energy and primary decomposition pathway for one of the candidate agents, CF<sub>3</sub>-CF<sub>3</sub>, involves dissociation of the C-C bond to form (two) •CF<sub>3</sub> radicals. These •CF<sub>3</sub> radicals will then react with methyl radicals, •CH<sub>3</sub>, which are present in significant concentrations in hydrocarbon flames. This radical-radical combination reaction has two decomposition channels whose relative importance is dependent upon temperature and pressure. One channel results in the formation of a fluoroethylene, CH<sub>2</sub>=CF<sub>2</sub> (and HF by-product). The other channel results in the formation of another fluoroethane, CH<sub>3</sub>-CF<sub>3</sub>. It is important that the mechanism adequately predicts the combustion products, the magnitude and rate of heat release in the flame, and ultimately the effectiveness of the added agent. Consequently, this requires that the mechanism also be able to describe correctly the decomposition of these two additional stable fluorinated hydrocarbon species (CH<sub>3</sub>-CF<sub>3</sub>, CH<sub>2</sub>=CF<sub>2</sub>). When one considers all decomposition channels for both the

candidate agents and their decomposition products, one essentially must include all chemistry describing almost all of the fluoromethanes and fluoroethanes.

Second, given that there are to date few experimental data with which to make comparisons, it is imperative to provide a level of self-consistency to this purely modeling work by considering a range of modeling parameters, including different reactor/flame geometries, different fuels, different (potential) agents, and many other conditions. In doing so, it allowed us to develop confidence in the validity of the qualitative trends that we observed. Quantitative prediction of the absolute or even relative effectiveness of the specific agents will require successful comparison of the simulations with experimental measurements.

## 1.2. Background

There has been a significant amount of work over many years that has investigated the effectiveness of halogenated fire suppressants, as well as other types of fire suppressants (see Bibliography section). We will not review this body of work, but refer the reader to these and other relevant sources. A large part of our work is based on the pioneering work in this area by Biordi and coworkers (*e.g.*, Biordi *et al.*, 1973), Dixon-Lewis (*e.g.*, Dixon-Lewis, 1977), Fristrom (*e.g.*, Fristrom and Van Tiggelen, 1979) and Westbrook (1983). In earlier experiments on a range of candidates,  $\text{CF}_3\text{Br}$  was identified as being very effective for extinguishing flames. However, the mechanism for inhibition by  $\text{CF}_3\text{Br}$  was not understood. Biordi and coworkers measured both stable and radical species in methane flames doped with  $\text{CF}_3\text{Br}$  using a flame-sampling molecular beam mass spectrometer. Many of the relevant elementary reactions that describe the decomposition of  $\text{CF}_3\text{Br}$ , its chemistry, and its influence on hydrocarbon flames were determined in this work. Westbrook developed the first comprehensive chemical mechanism to describe in detail the chemistry of  $\text{CF}_3\text{Br}$  and modeled inhibition in hydrocarbon flames. As a result of this work, it is generally agreed that flame suppression by bromine-containing compounds is a result of catalytic destruction of H atom species by Br atoms. The ability of bromine to recycle in the chemical system in the flame is directly related to the weak molecular bonds formed by bromine. Thus, bromine when complexed in molecules such as  $\text{CF}_3\text{Br}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{HBr}$ , and  $\text{Br}_2$ , can through a number of reactions regenerate Br atoms. It was

also determined in these studies that  $\bullet\text{CF}_3$ , formed by decomposition of  $\text{CF}_3\text{Br}$ , also removes H atoms by competition with radicals important to combustion (*e.g.*, H, O, OH,  $\text{HO}_2$ ).

There are a variety of ways in which fire suppressants act in inhibiting hydrocarbon flames. Most of these effects are intimately related. For example, a heat loss means a temperature decrease, which causes the chemistry to slow, which means fewer radicals leading to product formation, which means less heat generated, which results in a further temperature decrease and so on. One can separate suppression effects into two general categories: physical and chemical (although there is overlap). Chemical effects are directly related to the characteristics of the specific molecule (*e.g.*, H, F, or Cl substitution), while physical effects, in general, are not. For example, the heat capacity of a molecule is a physical effect, since to a first approximation it is largely a function of the number of atoms in the molecule and their connectivity but not the identity of the molecule (*i.e.*, its chemical composition).

There are a number of physical effects that relate to fluid mechanics, mass transport, and heat transport processes that were not specifically studied as a part of this modeling work. Physical effects that should be taken into account are, for example, PVT properties (pressure-volume-temperature), discharge dynamics, dispersion mechanics, as well as more complex flow reactor geometries than could be considered in this work. We will not discuss these physical effects in any detail here. However, it is necessary to understand the impact of these effects as they relate to our results in order to provide a framework for transfer of the results of our simulations to more realistic conditions. Some of the fluid mechanics and mass transport effects include dilution, turbulent mixing, diffusive mixing, thermal diffusion, and buoyancy. Heat related effects, which cannot directly be addressed in the simulations, include the latent heat of vaporization and non-adiabatic effects, such as radiative cooling or heat losses for flames attached to a cold surface.

There are a number of different types of chemical effects. Most of these involve different competing factors. First, all of the fluorinated hydrocarbons will eventually decompose and then burn (forming  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and HF). This liberates heat and increases flame temperatures (this speeds flame chemistry). On the other hand, the agents considered as replacements are large molecules with many atoms. Consequently, their high heat capacities may result in a decrease in flame temperature prior to complete combustion (this slows flame

chemistry). The competition between these two factors is strongly dependent upon conditions; most important of which is the mechanics of mixing of the fuel and the oxidizer. Another set of competing effects involves fluorinated radicals produced by agent decomposition. These radicals are slower to burn than their pure hydrocarbon analogues, because the C-F bond is significantly stronger than the C-H bond. Consequently, reactions involving these radicals may effectively compete with analogous pure hydrocarbon chemistry by creating less "flammable" intermediates, thereby inhibiting combustion of the hydrocarbon fuel. For example, since the agents are added to the air stream, their immediate decomposition products (radicals) are formed in oxygen-rich, relatively cold regions of the flame. Consequently, these radicals may be involved in termination steps, such as  $\cdot\text{CF}_3 + \text{HO}_2\cdot \rightarrow \text{CHF}_3 + \text{O}_2$ , slowing radical chain reactions and inhibiting the flame. These radicals also compete with hydrocarbon radicals for important H, O, and OH radicals. On the other hand, these radicals also react with stable molecules in the colder air stream (*e.g.*, O<sub>2</sub>), generating more radicals, such as O atoms, and thereby initiating chemistry or promoting combustion of the fuel.

### 1.3. Mechanism Development

We constructed a large comprehensive reaction set or "mechanism" for fluorinated hydrocarbon chemistry involving C<sub>1</sub> and C<sub>2</sub> stable and radical hydrocarbon species, including partially oxidized fluorinated hydrocarbons. The mechanism should be considered only a framework for future model development, rather than a finished product. Future refinements will require experimental validation by high-temperature flow reactor, premixed flame, and diffusion flame measurements, as well as measurements of important, yet currently uncertain rate constants.

### 1.4. Acknowledgments

The authors wish to acknowledge support of the project "Agent Screening for Halon 1301 Aviation Replacement" by the U.S. Naval Air Systems Command, the U.S. Army Aviation and Troop Command, the Federal Aviation Administration Technical Center, and the U.S. Air Force. This program at NIST was under the direction of Mr. Michael Bennett at the Wright

Patterson AFB Flight Dynamics Laboratory, Vehicle Subsystems Division, Survivability Enhancement Branch. The authors also wish to express their gratitude to Dr. Carl F. Melius of Sandia National Laboratories for use of the BAC (Bond Additivity Corrections) code.

## 2. Thermochemistry

### 2.1. Overview

Existing thermochemical data were compiled and evaluated. Where few or no data existed for potential species of interest (most of the radicals), we estimated that thermochemistry using both empirical methods, such as group additivity (Benson, 1976), and also through application of *ab initio* molecular orbital calculations (Melius, 1990; Curtiss *et al.*, 1991; Frisch *et al.*, 1992). In all cases (experimental, empirical, and *ab initio*), significant effort was made to utilize thermochemical data for each species that was consistent with data for all other species.

There are a number of general sources of relevant compiled and evaluated thermochemical data. These include *The Chemical Thermodynamics of Organic Compounds* (Stull *et al.*, 1969), *JANAF Thermochemical Tables* (Stull and Prophet, 1971; Chase *et al.*, 1985), *Thermochemical Data of Organic Compounds* (Pedley *et al.*, 1986), *TRC Thermodynamic Tables* (Rodgers, 1989), *Physical and Thermodynamic Properties of Pure Chemicals* (Daubert and Danner, 1985), and *NIST Structures and Properties Database and Estimation Program* (Stein *et al.*, 1991). There are two compilations/evaluations of fluorinated hydrocarbons in the *Journal of Physical and Chemical Reference Data*: "Ideal Gas Thermodynamic Properties of Six Fluoroethanes" (Chen *et al.*, 1975) and "Ideal Gas Thermodynamic Properties of Halomethanes" (Kudchadker and Kudchadker, 1978). There are two compilations/evaluations of fluorinated hydrocarbons in the *Russian Chemical Reviews*: "Thermochemistry of Halogenomethanes" (Kolesov, 1978) and "Thermochemistry of Haloethanes" (Kolesov and Papina, 1983). There are a few individual sources of more recent data for thermochemistry that are relevant. These include "Thermochemistry of Fluorocarbon Radicals" (Rodgers, 1978), "Hydrocarbon Bond Dissociation Energies" (McMillen and Golden, 1982), "A Kinetic Study of the Reactions of OH Radicals with Fluoroethanes. Estimates of C-H Bond Strengths in Fluoroalkanes" (Martin and Paraskevopoulos, 1983), and "Halomethylenes: Effects of Halogen Substitution on Absolute Heats of Formation" (Lias *et al.*, 1985). There are numerous other references with thermodynamic data for fluorinated hydrocarbons that we have compiled as part of this work. These are included in the Bibliography section and some of them will be cited and, possibly, be discussed in more detail in the relevant sections.

It should be noted that for some of the stable species and for many of the radicals, we have relied upon recent *ab initio* calculations of thermochemical data. This includes both *ab initio* calculations done as part of work and those done previously by other workers. Tschuikow-Roux and coworkers have calculated thermochemistry for the fluoroethyl radicals (Chen *et al.*, 1990a, 1990b; Chen *et al.*, 1991a, 1991b). Nyden (1993) has used *ab initio* calculations to obtain thermochemical data for a number of the fluoroethanes and fluoroethyl radicals. Details of our *ab initio* calculations can be found elsewhere (Burgess *et al.*, 1994; Zachariah *et al.*, 1995).

The thermochemical data that was used is given Tables 1-3 for hydrogen/oxygen and hydrocarbon species (Table 1), H/F species and C<sub>1</sub> fluorinated hydrocarbons (Table 2), and C<sub>2</sub> fluorinated hydrocarbons (Table 3). These tables include enthalpies of formation, entropies (at standard state), and temperature-dependent heat capacities. Comparisons between our calculated values (Zachariah *et al.*, 1995) and different literature values (experimental and estimated) for heats of formation are given in Table 4. Reported uncertainties in the literature values are also given in Table 4.

A discussion of the uncertainties in the thermochemical data is given in the text with each class of species. The literature values include those which have been calculated using *ab initio* methods. A critical evaluation of the *ab initio* values in comparison with experimentally derived values will be given in a future publication. In each case where the uncertainty in the data from the literature was not assigned, we have provided a value based on our limited evaluation of the data and typical uncertainties for that type of data.

The literature values for heats of formation consist of a number of different types of data. Many are good quality, experimentally derived values based on heat of combustion or heat of reaction data, where the other reactants and products have well-established heats of formation. The uncertainty in these data are typically less than 4 kJ/mol. Some of the data, although experimentally derived, have somewhat higher uncertainties due to side reactions or where the other reactants and products have somewhat uncertain heats of formation. Typically, these values have heats of formation with uncertainties of about 4-8 kJ/mol.

In some cases, the literature values are based, in whole or in part, on bond additivity, group additivity, or other trends in heats of formation of related species. Typically, these values have heats of formation with uncertainties of about 8-12 kJ/mol. Many of the radicals have literature values for their heats of formation that were determined using the heats of formation of the parent species and bond dissociation energies that were either indirectly measured or were reasonable estimates based on trends in other molecules. For example, Martin and Paraskevopoulos (1983) have estimated C-H bond strengths in fluoromethanes and fluoroethanes (and, consequently, heats of formations for the fluoromethyl and fluoroethyl radicals) through correlations between the rates of H atom abstraction by OH radicals, C-H vibrational frequencies, and known C-H bond strengths. We have supplemented these data with our own estimates in order to provide heats of formation for the other fluoroethyl radicals in the absence of other literature values.



## 2.2. H/O/F and Hydrocarbon Species

We used standard hydrogen/oxygen and hydrocarbon thermochemistry, most of which can be found in the JANAF tables (Stull and Prophet, 1971; Chase *et al.*, 1985) or in a Sandia compilation (Kee *et al.*, 1987), as can data for F and HF. There is a more recent value for the heat of formation of HF (Johnson *et al.*, 1973). However, we used the JANAF value for consistency, because many thermochemical and rate data for fluorinated species are based on the JANAF recommendation. More recent data on thermochemistry for C<sub>2</sub>H<sub>3</sub> and HCO have been utilized. Future mechanism refinements should include re-adjustment of any other thermochemistry (or rate constants) that are based upon older values for the heat of formation of these species.

Other simple species (*e.g.*, F<sub>2</sub>, FO•, HOF, FOF, FOO•, HOOF) were initially considered in the mechanism but were later excluded because they did not contribute to the overall chemistry.



## 2.3. C<sub>1</sub> Fluorinated Hydrocarbons

### 2.3.1. Fluoromethanes

We have chosen to employ heats of formation for the fluoromethanes recommended by Kolesov (1978) with the entropy and heat capacity data found in a review article (Rodgers *et al.*, 1974) in the Journal of Physical and Chemical Reference Data (JPCRD). We note that heats of formation for the fluoromethanes from our *ab initio* calculations (Zachariah *et al.*, 1995) using the BAC-MP4 method (Melius, 1990) are within about 2 kJ/mol of these recommended values.

There are a number of sources of compiled or evaluated thermochemical data for the fluoromethanes (CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub>, and CF<sub>4</sub>). Thermochemical data for the fluoromethanes has been reviewed by Lacher and Skinner (1968), by Stull *et al.* (1969), and by Cox and Pilcher (1970). Thermochemical data can also be found in the JANAF tables (Stull and Prophet, 1971), has been re-examined subsequently in JPCRD (Rodgers *et al.*, 1974), by Pedley *et al.* (1986), and mostly recently, by Gurvich, Veyts, and Alcock (1991). The most recent edition of the JANAF tables (Chase *et al.*, 1985) did not re-examine thermochemical data for the fluoromethanes. Recommendations for the heats of formation of the fluoromethanes have been also been made by Kolesov (1968). Gelles and Pitzer (1953) have tabulated entropy at standard state and heat capacity as a function of temperature for the fluoromethanes (and other halogenated methanes).

Heats of formation for CH<sub>2</sub>F<sub>2</sub> and CF<sub>4</sub> are the best known, with uncertainties of less than 1.5 kJ/mol, and are derived from their heats of combustion. The JPCRD recommended value for the heat of formation of CH<sub>2</sub>F<sub>2</sub> is based on a measurement by Neugebauer and Margrave (1958) of the heat of combustion of CH<sub>2</sub>F<sub>2</sub>. The heat of formation of CF<sub>4</sub> is based on measurements of a number of different heats of reactions involving CF<sub>4</sub> by Scott *et al.* (1955), Good *et al.* (1956), Neugebauer and Margrave (1956), Cox *et al.* (1965), Wood *et al.* (1967), Domalski and Armstrong (1967), and Greenberg and Hubbard (1968).

The heat of formation of CHF<sub>3</sub> has a slightly higher uncertainty (than for CH<sub>2</sub>F<sub>2</sub> and CF<sub>4</sub>) of about 4 kJ/mol due to side reactions (producing CF<sub>4</sub>) in its combustion. The JPCRD recommended value for the heat of formation of CHF<sub>3</sub> is based on a heat of combustion measurement by Neugebauer and Margrave (1958). The heat of formation of CHF<sub>3</sub> has also

been calculated using equilibrium data with  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$  as measured by Corbett *et al.* (1963), Goy *et al.* (1967), Coomber and Whittle (1967). The heat of formation of  $\text{CHF}_3$  can also be calculated assuming a heat of formation for  $\cdot\text{CF}_3$  and kinetic data (forward and reverse reactions) involving  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$  as measured by Coomber and Whittle (1966), Amphlett and Whittle (1968), and Goy *et al.* (1967), respectively.

The heat of formation of  $\text{CH}_3\text{F}$  has been estimated (with an uncertainty of about 10 kJ/mol) employing empirical trends in heats of formation of the other fluoromethanes, since there are no experimentally derived values (other than from appearance potential measurements). Although  $\text{CH}_3\text{F}$  is unlikely to be a key species in fluorinated hydrocarbon-inhibited hydrocarbon flames, as the simplest fluorinated hydrocarbon, its heat of formation is significant for benchmarking heats of formation of other fluorinated hydrocarbons. Empirical estimates for the heat of formation of  $\text{CH}_3\text{F}$  have also been made by Zahn (1934), Allen (1959), Bernstein (1965), Rodgers (1967), and Lacher and Skinner (1968). The recommended value in the JANAF tables (Stull and Prophet, 1971) is based on appearance potentials for  $\text{CH}_3^+$  from  $\text{CH}_3\text{F}$  measured by Lossing *et al.* (1954). Dibeler and Reese (1955) and Tsuda *et al.* (1964) have also measured roughly the same appearance potential.

### 2.3.2. Fluoromethyl Radicals

We have chosen to employ the heats of formation recommended by McMillen and Golden (1982). For entropies at standard state and heat capacity data, we used values for  $\cdot\text{CF}_3$  from the JANAF tables. Since (to our knowledge) no experimentally derived entropy and heat capacity data exist for  $\cdot\text{CH}_2\text{F}$  and  $\cdot\text{CHF}_2$ , we used that derived from our BAC-MP4 *ab initio* calculations. We note that the calculated heats of formation for the fluoromethyl radicals are within about 4 kJ/mol of the recommended experimental values.

There are a few sources of compiled or evaluated thermochemical data for the fluoromethyl radicals. Thermochemical data for the perfluoromethyl radical ( $\cdot\text{CF}_3$ ) can be found in the JANAF tables (Stull and Prophet, 1971) and have been re-examined subsequently by Rodgers (1978). The heat of formation of  $\cdot\text{CF}_3$  has an uncertainty of about 5 kJ/mol. Experimentally derived heats of formation (from bond dissociation energies and heat of reac-

tions) for all of the fluoromethyl radicals ( $\cdot\text{CH}_2\text{F}$ ,  $\cdot\text{CHF}_2$ ,  $\cdot\text{CF}_3$ ) can be found in evaluations by McMillen and Golden (1982) and Pickard and Rodgers (1983) with uncertainties of less than 10 kJ/mol.

The evaluated thermochemical data for  $\cdot\text{CH}_2\text{F}$  and  $\cdot\text{CHF}_2$  are based on a number of different experimental measurements. Okafo and Whittle (1974) have used heat of reaction data to determine the bond dissociation energy for  $\text{CHF}_2\text{-Br}$ , from which the heat of formation of  $\cdot\text{CHF}_2$  can be calculated. Martin and Paraskevopoulos (1983) have measured the rates of reaction of OH with some fluoromethanes and fluoroethanes and developed correlation between C-H bond dissociation energies, C-H stretching frequencies, and rates of abstraction of H atoms by OH radicals from fluoroalkanes. From heats of formation of the parent fluoromethanes and estimated C-H bond dissociation energies, one can determine values for the heats of formation of  $\cdot\text{CH}_2\text{F}$ ,  $\cdot\text{CHF}_2$ , and  $\cdot\text{CF}_3$ . Whittle and coworkers have used heat of reaction data to determine the bond dissociation energies of  $\text{CHF}_2\text{-H}$  and  $\text{CHF}_2\text{-Br}$  (Okafo and Whittle, 1974), from which the heat of formation of  $\cdot\text{CHF}_2$  can be calculated. Using kinetic data, bond dissociation energies for  $\text{CH}_2\text{F-H}$  have obtained by Pritchard and Perona (1969) and for  $\text{CHF}_2\text{-H}$  by Kerr and Timlin (1971), from which one can calculate the heats of formation of the corresponding radicals.

The evaluated thermochemical data for  $\cdot\text{CF}_3$  are based on a number of different experimental measurements. The heat of formation of  $\cdot\text{CF}_3$  has been calculated assuming a heat of formation for  $\text{CHF}_3$  and kinetic data (forward and reverse reactions) involving  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$ , as measured by Coomber and Whittle (1966), Amphlett and Whittle (1968), and Goy *et al.* (1967), respectively. It can also be calculated assuming a heat of formation of  $\text{CF}_3\text{I}$  and kinetic data for its reaction with  $\text{I}_2$ , as determined by Coomber and Whittle (1966). Pritchard and Thommarson (1964) used kinetic data from competing reactions to determine the  $\text{CF}_3\text{-H}$  bond dissociation energy and, consequently, the heat of formation of  $\cdot\text{CF}_3$  can be calculated assuming a heat of formation for  $\text{CHF}_3$ . Whittle and coworkers have used heat of reaction data to determine the bond dissociation energies for  $\text{CF}_3\text{-CF}_3$  (Coomber and Whittle, 1967),  $\text{CF}_3\text{-Br}$  (Ferguson and Whittle, 1972), and  $\text{CF}_3\text{-I}$  (Okafo and Whittle, 1975), from which the heat of formation of  $\cdot\text{CF}_3$  can be calculated. Tsang (1986) has determined a value for the heat of

formation of  $\cdot\text{CF}_3$  based on the bond dissociation energy of  $\text{CF}_3\text{-Br}$  from shock tube decomposition studies.

### 2.3.3. Fluoromethylenes and Fluoromethylidyne Radical

We used heats of formation for  $:\text{CF}_2$  as adopted by Rodgers (1978) and for  $:\text{CHF}$  as provided by Pritchard *et al.* (1984). For entropies at standard state and heat capacity data of both species, we used values from the JANAF tables. We note that heats of formation for both species from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995) are within about 15 kJ/mol of the recommended experimental values.

There are a few sources of thermochemical data for the closed-shell fluoromethylenes ( $:\text{CHF}$  and  $:\text{CF}_2$ ). Thermochemical data for these species can be found in the JANAF tables (Stull and Prophet, 1971). More recently, Rodgers (1978) has recommended a value for the heat of formation of  $:\text{CF}_2$  based largely upon kinetic data. Hsu *et al.* (1978) and Pritchard *et al.* (1984) have independently made a recommendation for the heat of formation of  $:\text{CHF}$  based upon heat of reaction and kinetic data. Lias *et al.* (1985) have provided values for the heat of formation of both  $:\text{CHF}$  and  $:\text{CF}_2$  based upon appearance and ionization potentials. Unfortunately (since  $:\text{CHF}$  and  $:\text{CF}_2$  are important species), there are significant uncertainties in their heats of formation. The values for  $:\text{CF}_2$  are the best ( $\pm 10$  kJ/mol) and are derived from a number of different types of measurements. The uncertainty in the heat of formation for  $:\text{CHF}$  is even greater ( $\pm 30$  kJ/mol) due to the lack of direct, reliable data.

The experimental data for the heat of formation of  $:\text{CF}_2$  comes from a number of different measurements. The heat of formation of  $:\text{CF}_2$  has been calculated from heat of reaction or kinetic data from the decomposition of  $\text{C}_2\text{F}_4$  by Modica and LaGraff (1965, 1966), by Zmbov *et al.* (1968), by Schug and Wagner (1968), and by Carlson (1971). Using equilibrium data in experiments by Farber *et al.* (1969), one can also determine a value. The heat of formation of  $:\text{CF}_2$  has also been calculated from the decomposition of various halomethanes: from the decomposition of  $\text{CHF}_3$  by Schug and Wagner (1978), from the decomposition of  $\text{CHF}_2\text{Br}$  by Okafo and Whittle (1974), and from the decomposition of  $\text{CHF}_2\text{Cl}$  by Dalby (1964), Gozzo and Patrick (1964), Edwards and Small (1965), and Schug and Wagner (1968). The ionization

potential of :CF<sub>2</sub> has been used to estimate its heat of formation by Fisher *et al.* (1965), Pottie (1965), and Zmbov *et al.* (1968). Various appearance potential measurements by Walter *et al.* (1969), Berman *et al.* (1981), and Paulino and Squires (1991) have also been used to estimate a value for the heat of formation of :CF<sub>2</sub>. The ionization and appearance potential measurements have been reviewed in detail by Lias *et al.* (1985) and Paulino and Squires (1991).

Thermochemical data for fluoromethylidyne ( $\bullet$ CF) can be found in the JANAF tables (Stull and Prophet, 1971). More recently, Gurvich *et al.* (1991) have also provided thermochemical data for  $\bullet$ CF. In the latter review, more recent measurements by Hildenbrand (1975) were also considered, in addition to earlier measurements by Modica (1966) and Farber *et al.* (1969). We used the more recent value from Gurvich *et al.* (1991) for the heat of formation with the entropy and heat capacity data provided in the JANAF tables. The reported uncertainties in the heat of formation are about 10 kJ/mol. We note that our BAC-MP4 *ab initio* heat of formation for  $\bullet$ CF is within about 10-20 kJ/mol of the recommended values.

#### 2.3.4. Carbonyl Fluorides and Fluoromethoxy Radicals

Thermochemical data for the carbonyl fluorides (CHF=O, CF<sub>2</sub>=O,  $\bullet$ CF=O) can be found in the JANAF table. We have employed these data. The uncertainty in the heat of formation of CF<sub>2</sub>=O is reported to be about 2 kJ/mol. For the other two carbonyl fluorides, where there is little or no experimental data, the estimated uncertainty in their heats of formation are probably at least 15 kJ/mol.

Gurvich *et al.* (1991) have recommended a value for the heat of formation of  $\bullet$ CF=O that is similar to the JANAF recommendation (about 8 kJ/mol higher). This recommendation is based upon appearance potential measurements of McNeil and Thynee (1969) and heat of reaction measurements by Heras *et al.* (1962).

We note that heats of formation for these species from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995) are within about 20 kJ/mol of the recommended experimental values, except for CF<sub>2</sub>=O, where the *ab initio* value is about 40 kJ/mol higher. Other *ab initio* calculations (Montgomery *et al.*, 1994; Schnieder and Wallington, 1994) using different approaches also predict a heat of formation for CF<sub>2</sub>=O that is higher (by about 30

kJ/mol) than the experimental value. Because of this significant difference, both uncertainties in the experimental measurements and *ab initio* calculations warrant further examination.

The biggest uncertainties here are for CHF=O ( $\pm 20$  kJ/mol) and  $\cdot$ CF=O ( $\pm 10$  kJ/mol), where there are little or no direct experimental data available and, consequently, their heats of formation were estimated (Stull and Prophet, 1971) using average bond dissociation energies from other related compounds. Given that reliable experimental data exists for the unimolecular decomposition of CHF=O (Saito *et al.*, 1985), uncertainty in its heat of formation may be unimportant. However, under some conditions the bimolecular reaction  $\cdot$ CF=O + H<sub>2</sub>O → CHF=O + OH (roughly 80 kJ/mol endothermic) may contribute. Consequently, uncertainty in the heat of formation of CHF=O may play some role. In contrast, the heat of formation of  $\cdot$ CF=O is very important, since there are not experimental data for its unimolecular decomposition, which is a primary decomposition pathway (competing with H atom combination followed by HF elimination).

We used an experimentally derived value for the heat of formation of the perfluoromethoxy radical CF<sub>3</sub>O $\cdot$  (Batt and Walsh, 1982) with a reported estimated uncertainty of about 6 kJ/mol. For entropy at standard state and heat capacity data, we used that derived from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995). The heat of formation of CF<sub>3</sub>O $\cdot$  from the *ab initio* calculations is within about 30 kJ/mol of the experimentally derived value.

A number of other species, such as the other fluoromethoxy radicals (CH<sub>2</sub>FO $\cdot$ , CHF<sub>2</sub>O $\cdot$ ), fluoromethanols (*e.g.*, CF<sub>3</sub>OH), or fluoromethylperoxy radicals (*e.g.*, CF<sub>3</sub>OO $\cdot$ ), were initially considered in the mechanism (using *ab initio* thermochemical data). These species were later excluded, because they did not contribute to the overall chemistry. In many cases, these species were present in steady state concentrations and, consequently, the creation and destruction reactions could be combined into a single overall reaction. Although these species may be important in atmospheric chemistry, they are present in extremely low concentrations at high temperatures in hydrocarbon/air flames.

## 2.4. C<sub>2</sub> Fluorinated Hydrocarbons

### 2.4.1. Fluoroethanes

We chose to use thermochemical data from a Journal of Physical and Reference Data (JPCRD) review (Chen *et al.*, 1975) for the six simple fluoroethanes (CH<sub>3</sub>-CH<sub>2</sub>F, CH<sub>3</sub>-CHF<sub>2</sub>, CH<sub>3</sub>-CF<sub>3</sub>, CH<sub>2</sub>F-CF<sub>3</sub>, CHF<sub>2</sub>-CF<sub>3</sub>, CF<sub>3</sub>-CF<sub>3</sub>). For CH<sub>2</sub>F-CH<sub>2</sub>F, we used a heat of formation calculated using the C-C bond dissociation energy as determined by Kerr and Timlin (1971) and the heat of formation for •CH<sub>2</sub>F as recommended by McMillen and Golden (1982). We used the heat of formation of CH<sub>2</sub>F-CHF<sub>2</sub> as recommended by Lacher and Skinner (1968). For CHF<sub>2</sub>-CHF<sub>2</sub>, we used a heat of formation calculated using the C-C bond dissociation energy as determined by Millward *et al.* (1971) and the heat of formation for •CHF<sub>2</sub> as recommended by McMillen and Golden (1982). Standard state entropy and heat capacities for these other 3 fluoroethanes were computed based on vibrational frequencies and moments of inertia from our *ab initio* calculations. We note that heats of formation for all of the fluoroethanes from our BAC-MP4 *ab initio* calculations are within about 10-20 kJ/mol of the recommended experimental or empirical values.

We believe some re-examination of all of the heat of formation data is warranted. For example, the heat of formation of CH<sub>3</sub>-CF<sub>3</sub> recommended in the JPCRD review is based on old values for •CH<sub>3</sub> and •CF<sub>3</sub>. In addition, employing a group additivity scheme with an ionic correction should yield better values for both CH<sub>2</sub>F-CH<sub>2</sub>F and CHF<sub>2</sub>-CHF<sub>2</sub>.

There are a number of sources of compiled or evaluated data for the fluoroethanes. Thermochemical data for some of the fluoroethanes can be found in JPCRD (Chen *et al.*, 1975) and the DIPPR compilation (Daubert and Danner, 1985). Recommendations for the heats of formation of some of the fluoroethanes have been made by Kolesov and Papina (1983) and by Pedley *et al.* (1986). There are no experimentally derived heats of formation for two of the fluoroethanes (CH<sub>3</sub>-CH<sub>2</sub>F, CH<sub>2</sub>F-CF<sub>3</sub>). These have been estimated using bond additivity, group additivity, or other trends in heats of formation. However, there are significant uncertainties in using these procedures, because of non-covalent or ionic contributions to the stability of these species due to the high electronegativity of fluorine. For example, CH<sub>3</sub>-CF<sub>3</sub> is about 33 kJ/mol more stable than predicted using heats of formation of CH<sub>3</sub>-CH<sub>3</sub> and CF<sub>3</sub>-CF<sub>3</sub>. All three of these

species have heats of formation that were derived from good quality experimental measurements. The additional stabilization can be rationalized as an ionic contribution to the C-C bond strength because of large differences in net charges on the carbon atoms of the -CH<sub>3</sub> and -CF<sub>3</sub> groups due to the high electronegativity of the F atoms.

There are a number of different sources of experimental data for the heats of formation of the fluoroethanes. These various sources are described in the paragraphs below.

The heat of formation of ethyl fluoride (CH<sub>3</sub>-CH<sub>2</sub>F) has been estimated (Chen *et al.*, 1975) using group additivity and heat of reaction data for propyl fluoride (Lacher *et al.*, 1956). A recommendation for the heat of formation of ethyl fluoride (CH<sub>3</sub>-CH<sub>2</sub>F) has recently been given by Luo and Benson (1988) based on electronegativity correlations of heats of formation of substituted alkanes and is significantly lower (15 kJ/mol) than other recommendations. The reasons for this significant difference warrant further examination. CH<sub>3</sub>-CH<sub>2</sub>F is unlikely to be important as a species in the fluorocarbon-inhibited hydrocarbon flames. However, as a simple, single-substituted fluorinated hydrocarbon (like CH<sub>3</sub>F), its heat of formation is important as a reference point for the heats of formation of other species. For example, another -CH<sub>2</sub>F substituted fluoroethane, CH<sub>2</sub>F-CF<sub>3</sub>, has no experimentally derived heats of formation. Any uncertainties in the heats of formation and, consequently, stability of the fluoroethanes will influence product channels for fluoromethyl combinations (*e.g.*, •CH<sub>3</sub> + •CF<sub>3</sub> → CH<sub>3</sub>-CF<sub>3</sub> versus •CH<sub>3</sub> + •CF<sub>3</sub> → CH<sub>2</sub>=CF<sub>2</sub> + HF).

Kolesov *et al.* (1968) have measured the heat of combustion of CH<sub>3</sub>-CHF<sub>2</sub>, from which one can calculate its heat of formation. The heat of formation of CH<sub>3</sub>-CHF<sub>2</sub> could be determined from the enthalpy of hydrogenation of CF<sub>2</sub>=CCl<sub>2</sub> as measured by Lacher *et al.* (1956) given a reliable value for the heat of formation of CF<sub>2</sub>=CCl<sub>2</sub> could be obtained.

We calculated a heat of formation for CH<sub>2</sub>F-CH<sub>2</sub>F based on the C-C bond dissociation energy (368.6 kJ/mol) as determined by Kerr and Timlin (1971) and the heat of formation for •CH<sub>2</sub>F (-32.6 kJ/mol) as recommended by McMillen and Golden (1982). The bond dissociation energy was determined from the critical energy (E<sub>0</sub>) calculated using RRKM analysis of experimental kinetic data for thermal (Chang and Setser, 1969) and chemically activated decomposition of CH<sub>2</sub>F-CH<sub>2</sub>F.

Kolesov *et al.* (1965) have determined a heat of formation for  $\text{CH}_3\text{-CF}_3$  by measuring its heat of combustion. Kinetic data for the forward and reverse reactions for  $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightleftharpoons \text{CH}_3\text{-CF}_3$  can be used to obtain a heat of formation for 1,1,1-trifluoroethane. Kinetic data for this reaction have been obtained by Giles and Whittle (1965), Pritchard and Perona (1970), and Chang *et al.* (1972). These data have been reviewed by Rodgers and Ford (1973).

The heat of formation of  $\text{CH}_2\text{F-CHF}_2$  has been determined (Kolesov and Papina, 1983) from the enthalpy of hydrogenation of  $\text{CF}_2=\text{CFCI}$  as measured by Lacher *et al.* (1956).

We have calculated a heat of formation for  $\text{CHF}_2\text{-CHF}_2$  based on the C-C bond dissociation energy (382.4 kJ/mol) as determined by Millward *et al.* (1971) and the heat of formation for  $\cdot\text{CHF}_2$  (-247.7 kJ/mol) as recommended by McMillen and Golden (1982). The bond dissociation energy was set equal to the activation energy for thermal decomposition of  $\text{CHF}_2\text{-CHF}_2$ , which was determined from analysis of experimental kinetic data.

The heat of formation of  $\text{CHF}_2\text{-CF}_3$  can be obtained from equilibrium data with  $\text{CF}_3\text{-CF}_2\text{Br}$  (and group additivity) as measured by Whittle and coworkers (Coomber and Whittle, 1967; Ferguson and Whittle, 1972) and from heat of reaction data for the bromination of  $\text{CF}_2=\text{CF}_2$  (and group additivity) as measured by Lacher *et al.* (1956). In addition, one can calculate a value for the heat of formation for  $\text{CHF}_2\text{-CF}_3$  from the heat of formation of the perfluoroethyl radical ( $\text{CF}_3\text{-CF}_2\cdot$ ) and the  $\text{CF}_3\text{CF}_2\text{-H}$  bond dissociation energy. Wu and Rodgers (1976) determined the heat of formation of the perfluoroethyl radical by measuring the enthalpy of its reaction with  $\text{I}_2$ . Values for the bond dissociation energy of  $\text{CF}_3\text{CF}_2\text{-H}$  have been determined by Bassett and Whittle (1972) and Martin and Paraskevopoulos (1983).

The heat of formation of  $\text{CF}_3\text{-CF}_3$  has been determined from equilibrium data with  $\text{CF}_3\text{Br}$  as measured by Coomber and Whittle (1967), with  $\text{CF}_3\text{-CN}$  as measured by Walker *et al.* (1970), and with  $\text{CF}_4$  (and  $\text{NF}_3$  as the oxidizer) as measured by Sinke (1966).

#### 2.4.2. Fluoroethyl Radicals

In the absence of reliable experimental data, we used the calculated thermochemical data for the fluoroethyl radicals as provided by Tschuikow-Roux and coworkers (Chen *et al.*, 1990a, 1990b; Chen *et al.*, 1991a, 1991b) for consistency. However, we believe some re-examination

of all of the heat of formation data (both experimental and *ab initio*) is warranted. For the radical CH<sub>3</sub>-CHF•, we used the average of the heats of formation reported by Martin and Paraskevopoulos (1983) and Tschuikow-Roux and Salomon (1987). For the three fluoroethyl radicals, CH<sub>2</sub>F-CHF•, CHF<sub>2</sub>-CF<sub>2</sub>•, and CF<sub>3</sub>-CHF•, we calculated heats of formation based on C-H bond dissociation energies determined by Martin and Paraskevopoulos (1983). We note that heats of formations for the fluoroethyl radicals from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995) are within about 10-20 kJ/mol of the recommended literature values.

There are a number of sources of heats of formation for the fluoroethyl radicals. There are experimentally derived thermochemical data (Rodgers, 1978) for a few of the fluoroethyl radicals (CH<sub>3</sub>-CF<sub>2</sub>•, CF<sub>3</sub>-CH<sub>2</sub>•, CF<sub>3</sub>-CF<sub>2</sub>•). Heats of formation for the others have been estimated using heats of formation for the fluoroethanes and C-H or C-F bond dissociation energies for CH<sub>3</sub>-CHF• and CF<sub>3</sub>-CHF• by Martin and Paraskevopoulos (1983), for CH<sub>3</sub>-CHF• by Tschuikow-Roux and Salomon (1987), and for all of the other fluoroethyl radicals by Burgess and Zachariah (this work). Thermochemistry for all of the fluoroethyl radicals have been calculated using *ab initio* molecular orbital theory by Tschuikow-Roux and coworkers (cited above). They used the experimentally derived heats of formation of the 3 fluoroethyl radicals recommended by Rodgers (1978). For the others, they used their calculated energies in conjunction with isodesmic-homodesmic reactions (with known experimental reaction enthalpies) to provide values that approach the "true" heats of formation.

#### 2.4.3. Fluoroethylenes and Fluorovinyl Radicals

We used the heat of formation of CH<sub>2</sub>=CHF as recommended by Gurvich *et al.* (1991). Entropy at standard state and heat capacity data were taken from the DIPPR compilation (Daubert and Danner (1985). These data can also be found in the TRC Thermodynamic Tables (1990). The heat of formation data are based on measurements by Kolesov and Papina (1970) of the heat of combustion of vinyl fluoride. Pedley *et al.* (1986) have also made a recommendation based on this experimental data. A heat of formation was also determined by Williamson *et al.* (1976) based on appearance potential measurements.

We have chosen to use heats of formation for  $\text{CHF}=\text{CHF}(E)$  and  $\text{CHF}=\text{CHF}(Z)$  based on appearance ionization potential measurements by Stadelman and Vogt (1980) and entropies at standard state and heat capacities based on geometries and vibrational frequencies from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995). Gurvich *et al.* (1991) have also estimated heats of formation for these species using a bond additivity method. For  $\text{CH}_2=\text{CF}_2$ , we used the heat of formation recommended by Gurvich *et al.* (1991) with entropy at standard state and heat capacity data taken from Stull *et al.* (1969). Recommendations for the heat of formation for 1,1-difluoroethylene have also been made by Lacher and Skinner (1968), Stull *et al.* (1969), Cox and Pilcher (1970), and Pedley *et al.* (1970). All of these recommendations are based on heat of combustion measurements by Neugebauer and Margrave (1956) and Kolesov *et al.* (1962).

We used thermochemical data for  $\text{CHF}=\text{CF}_2$  as recommended by Gurvich *et al.* (1991). The heat of formation data is based on an experimental measurement by Kolesov *et al.* (1962) of the heat of combustion of trifluoroethylene. Recommended values (also based on these experiments) can be found in the evaluations of Stull *et al.* (1969), Cox and Pilcher (1970), and Pedley *et al.* (1986).

We used thermochemical data for  $\text{CF}_2=\text{CF}_2$  from the JANAF tables (Stull and Prophet, 1971). The recommended heat of formation is based the heat of reaction data for conversion to amorphous carbon by Neugebauer and Margrave (1956) and Kolesov *et al.* (1962). Lacher and Skinner (1968), Stull *et al.* (1969), Cox and Pilcher (1970), Kolesov and Papina (1983), Pedley *et al.* (1986), and Gurvich *et al.* (1991) have all reviewed the existing experimental data and made recommendations. These evaluations were made based upon a number of different sources of experimental heat of reaction data for perfluoroethylene, including the data of Lacher *et al.* (1949), Lacher *et al.* (1950), Kirkbride and Davidson (1954), von Wartenberg and Schiefer (1955), Duus (1955), Neugebauer and Margrave (1956), Lacher *et al.* (1956), Scott *et al.* (1956), Kolesov *et al.* (1962), and Edwards and Small (1964).

We note that the heats of formation for the fluoroethylenes that we have calculated using the BAC-MP4 *ab initio* method are within about 10 kJ/mol of the recommended experimental values.

There are not any experimentally derived thermochemical data (to our knowledge) for the fluorovinyl radicals, other than the heat of formation for  $\text{CF}_2=\text{CF}\cdot$ . The heat of formation of the perfluorovinyl radical has been estimated by Bryant (1962) based on trends in C-F bond dissociation energies for perfluorocarbons. Gurvich *et al.* (1991) recommended a value based on a review of appearance potential measurements by Thynee and MacNeil (1970), Lifshitz and Crajower (1972), and Bibby and Caster (1966). Because of the lack of experimental data for most of the fluorovinyl radicals, we chose to use thermochemical data from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995) in order to provide a consistent set. We note that our calculated value is within about 10 kJ/mol of the experimentally derived value that was recommended by Gurvich *et al.* (1991).

#### 2.4.4. Fluoroacetylenes, Fluoroketenes, and Fluoroketyl Radical

Data on the thermochemistry of the fluoroacetylenes ( $\text{C}_2\text{HF}$ ,  $\text{C}_2\text{F}_2$ ) can be found in the JANAF tables (Stull and Prophet, 1971), however, with relatively large uncertainties:  $\pm 60$  kJ/mol and  $\pm 20$  kJ/mol in the heats of formation, respectively. Fluoroketenes ( $\text{CHF}=\text{C}=\text{O}$  and  $\text{CF}_2=\text{C}=\text{O}$ ) and the fluoroketyl radical ( $\cdot\text{CF}=\text{C}=\text{O}$ ) can be formed through a number of channels. These channels are analogous to those considered in pure hydrocarbon chemistry for ketene ( $\text{CH}_2=\text{C}=\text{O}$ ). To assess the importance of the fluoroketene species and relevant reactions, we included these species in the mechanism. There are not any experimentally derived data for these species. Consequently, we used data from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995).

A number of other partially oxidized species, such as  $\text{CH}_3\text{-CFO}$ , were excluded from the mechanism based on the assumption that they would be only present in steady state concentrations at flame temperatures. For lower temperatures, these species may become important and, consequently, our assumption should be re-examined. It is possible that perfluoro-oxidized species, such as  $\text{CF}_3\text{-CFO}$ , may be present at flame temperatures. For example, since both  $\cdot\text{CF}_3$  and  $\cdot\text{CFO}$  are present in significant concentrations, the combination of these species (and stabilization) may be a source of  $\text{CF}_3\text{-CFO}$ . This should be examined in future refinements of this mechanism.

## 2.5. BAC-MP4 *Ab Initio* Predictions

For a number of species considered in the reaction set, especially the radicals, there are little or no thermochemical data. Consequently, we have estimated that data using BAC-MP4 *ab initio* calculations (see description below). In order to quantify the uncertainties in the calculated data, we have also performed calculations on many related species where there is good quality experimental data.

Structures, energies, and thermochemical data for a large number of C<sub>1</sub> and C<sub>2</sub> hydrocarbons, oxidized hydrocarbons, hydrofluorocarbons, and oxidized hydrofluorocarbons, including radical species, were calculated using the BAC-MP4 procedure as outlined by Melius (1986). This procedure involves *ab initio* molecular orbital calculations using the Gaussian series of programs (Frish *et al.*, 1990), followed by application of a bond additivity correction (BAC) procedure to the *ab initio* calculated energies. The BAC procedure enables energies to be calculated at accuracies that are necessary for chemical applications, without the need to resort to large basis sets or configuration interaction terms. This is a particularly important issue when the goal is the generation of a sufficiently complete data set necessary for development of a detailed chemical mechanism.

Equilibrium geometries, vibrational frequencies, and zero point energies were calculated at the Hartree-Fock level using a 6-31G(d) basis set (HF/6-31G\*). Using these geometries, single point energies were calculated with 4th order Moller-Plesset theory using a 6-31G(d,p) basis set (MP4/6-31G\*\*), to which the BAC procedure was applied. In the BAC method, errors in the electronic energy of a molecule are bond-wise additive and depend on bonding partner, distance, and next-nearest neighbors. The energy per bond is corrected by calibration at a given level of theory against molecules of known energy.

Table 4 lists calculated heats of formation for most of the species in the reaction set, as well as literature values (where available). We note that we have calculated thermochemical data for a number of related species that are not included in the reaction set. These data are also included in Table 4 for purposes of comparison. Of the approximately 110 species, where we have calculated heats of formation, about 70 species have literature values. We note that the

literature values consist of a number of different types of data, including estimated and calculated values, in addition to those that are derived from experimental measurements.

The average difference between the BAC-MP4 and the literature values is about 9.5 kJ/mol, while the standard deviation is about 7.5 kJ/mol. From these data, we conclude that for the fluorinated hydrocarbon system, that heats of formation calculated using the BAC-MP4 method provide values that are accurate to less than 10 kJ/mol or comparable to the majority of the experimentally derived values. We believe that the precision of the *ab initio* values for any homologous series to be significantly better than that which is typically obtainable from experimental measurements. This becomes evident when calculated bond dissociation energies are compared to those derived from experimental measurements. A more detailed discussion and comparison can be found elsewhere (Zachariah *et al.*, 1995).

Of all the species,  $\text{CF}_2=\text{O}$  has the largest difference between calculated and experimental values. Although the quoted uncertainty for this molecule is small, there is reason to believe that the experimental data may have had side reactions complicating its determination. In addition, other recent calculations (Schnieder and Wallington, 1994; Montgomery *et al.*, 1994) using other *ab initio* methods predict a heat of formation for  $\text{CF}_2=\text{O}$  that is consistent with our BAC-MP4 calculated value. There are a number of other oxyfluoro-species that have significant differences between calculated and literature values. However, the heats of formation of these species were derived based on heats of reactions involving  $\text{CF}_2=\text{O}$ . Consequently, if the true value for  $\text{CF}_2=\text{O}$  was closer to the calculated value, then the experimentally derived values for these other species would also be closer to their respective calculated values.

There are a number of other species with significant differences between calculated and literature values. The uncertainties in many of these literature values are high because they are only indirectly tied to experimental measurements. For example, the heat of formation of the  $\text{HCOO}\cdot$  radical is an estimate based on group additivity. The heats of formation of two fluoroethyl radicals ( $\text{CF}_3\text{-CHF}\cdot$  and  $\text{CH}_2\text{F-CF}_2\cdot$ ) were determined from estimated from C-H bond dissociation energies based on correlations between rates of H atom abstractions, C-H bond frequencies, and known C-H bond strengths.

To reiterate, from analysis of the data presented in Table 4, we can conclude that for the fluorinated hydrocarbon system, that heats of formation calculated using the BAC-MP4 method

provide values that are accurate to less than 10 kJ/mol or comparable in accuracy to the majority of the experimentally derived values. Furthermore, from trends in bond dissociation energies, we believe that the precision of the *ab initio* values for any homologous series to be significantly better than that which is typically obtainable from experimental measurements.



**TABLE 1. Enthalpy of Formation, Entropy, Heat Capacities for H/O, Hydrocarbons**

SPECIES	$\Delta H^\circ_f(298)$ kJ/mol	$S^\circ(298)$ J/mol/K	$C_p^\circ(T)$ J/mol/K								Ref
			300	500	800	1000	1200	1500	2000	3000	
N <sub>2</sub>	0.0	191.5	29.07	29.63	31.39	32.76	33.70	34.80	35.98	37.02	a
H <sub>2</sub>	0.0	130.6	28.87	29.27	29.58	30.16	31.07	32.35	34.23	37.11	a
O <sub>2</sub>	0.0	205.0	29.33	31.11	33.75	34.93	35.59	36.49	37.78	39.84	a
H <sub>2</sub> O	-241.8	188.7	33.46	35.33	38.58	41.31	43.87	47.10	51.14	55.77	a
H <sub>2</sub> O <sub>2</sub>	-136.1	232.9	43.57	51.65	59.80	63.64	66.75	70.50	74.80	78.91	a
H	218.0	114.6	20.78	20.78	20.78	20.78	20.78	20.78	20.78	20.78	a
O	249.2	160.9	21.89	21.25	20.98	20.91	20.88	20.84	20.82	20.94	a
OH	39.0	183.6	29.93	29.57	29.84	30.68	31.66	32.94	34.63	36.76	a
HO <sub>2</sub>	10.5	229.0	34.87	39.69	45.10	47.64	49.59	52.10	55.33	59.10	a
CH <sub>4</sub>	-74.9	186.0	35.26	46.60	62.75	72.15	78.71	86.32	94.49	101.36	a
•CH <sub>3</sub>	145.7	194.0	38.62	45.33	53.85	59.07	63.19	68.06	73.45	78.30	a
<sup>1</sup> :CH <sub>2</sub>	387.0	195.5	34.50	37.15	41.57	44.21	46.36	49.11	52.45	55.33	a
<sup>3</sup> :CH <sub>2</sub>	424.7	188.7	33.79	36.00	41.20	44.38	46.63	49.48	52.88	55.58	a
•CH	594.1	182.9	29.09	29.49	30.82	32.56	34.38	36.61	39.18	41.44	a
C <sub>2</sub> H <sub>6</sub>	-83.9	229.0	52.61	77.89	108.05	122.59	132.68	144.83	158.64	171.05	a
C <sub>2</sub> H <sub>5</sub> •	117.2	251.6	47.37	66.73	94.48	106.71	114.07	123.66	135.76	146.83	a
C <sub>2</sub> H <sub>4</sub>	52.5	219.2	42.82	62.52	83.90	94.17	101.38	109.70	118.54	125.81	a
C <sub>2</sub> H <sub>3</sub> •	294.5	227.9	45.77	57.82	71.91	78.77	83.27	89.21	96.90	104.31	a
C <sub>2</sub> H <sub>2</sub>	226.7	200.9	44.44	54.73	63.90	68.23	71.97	76.46	81.65	87.09	a
CH <sub>3</sub> OH	-201.1	239.6	43.98	59.64	79.80	89.53	96.40	104.66	114.00	121.99	a
CH <sub>3</sub> O•	16.3	228.5	37.99	52.02	69.58	77.81	83.38	90.00	97.32	103.23	a
•CH <sub>2</sub> OH	-17.2	246.3	47.38	60.16	73.37	78.62	82.59	87.65	93.73	98.76	a
CH <sub>2</sub> O	-115.9	218.6	35.15	43.94	55.90	62.27	66.34	70.99	75.80	79.54	a
•CHO	43.5	224.5	34.49	38.81	44.93	48.20	50.22	52.53	54.96	57.04	a
CO	-110.5	197.5	29.08	29.85	31.86	33.25	34.15	35.17	36.27	37.21	a
CO <sub>2</sub>	-393.5	213.7	37.28	44.56	51.54	54.36	56.20	58.29	60.43	62.19	a
CH <sub>2</sub> CO	-51.9	241.8	52.01	65.54	78.63	84.70	88.88	93.89	99.49	104.15	a
•CHCO	177.6	254.1	52.93	59.53	67.25	70.43	72.56	75.24	78.39	80.77	a
HCCOH	85.5	245.6	55.30	67.62	80.10	84.94	88.59	93.24	98.81	103.38	a

**TABLE 2. Enthalpy of Formation, Entropy, Heat Capacities for H/F/O, C<sub>1</sub> Fluorocarbons**

SPECIES	$\Delta H^\circ_f(298)$ kJ/mol	$S^\circ(298)$ J/mol/K	$C_p(T)$ J/mol/K								Ref
			300	500	800	1000	1200	1500	2000	3000	
F <sub>2</sub>	0.0	202.7	31.37	34.34	36.46	37.19	37.66	38.20	38.87	39.87	a
HF	-272.5	173.7	29.12	29.20	29.55	30.14	30.98	32.25	34.01	36.21	a
F	78.9	158.7	22.77	22.10	21.46	21.25	21.14	21.03	20.93	20.84	a
CH <sub>3</sub> F	-232.6	222.8	37.50	51.26	68.90	77.30	83.34	90.21	96.81	102.59	b
CH <sub>2</sub> F <sub>2</sub>	-452.2	246.6	42.96	58.91	76.33	83.55	88.84	94.35	99.47	103.97	b
CHF <sub>3</sub>	-697.6	259.6	51.15	69.26	85.10	91.01	94.89	98.83	102.42	105.39	b
CF <sub>4</sub>	-933.0	261.3	61.30	80.67	94.49	98.73	101.41	103.67	105.52	106.90	b
•CH <sub>2</sub> F	-32.6	234.4	38.71	48.67	59.29	64.20	67.92	72.02	76.06	79.71	c,d
•CHF <sub>2</sub>	-247.7	256.0	42.21	54.10	65.33	69.66	72.60	75.69	78.47	80.92	c,e
•CF <sub>3</sub>	-467.4	265.0	49.94	63.30	73.24	76.37	78.27	79.92	81.29	82.30	c,e
:CHF	163.2	223.2	34.63	39.25	45.21	47.93	50.05	52.43	55.43	61.04	f,e
:CF <sub>2</sub>	-186.6	240.7	39.01	46.45	52.35	54.18	55.28	56.31	57.14	58.37	g,e
•CF	242.1	212.9	30.05	32.24	34.79	35.77	36.32	36.96	37.53	38.20	p
CHF=O	-376.6	246.7	40.50	51.65	63.12	67.92	71.20	74.70	77.94	80.67	d
CF <sub>2</sub> =O	-638.9	258.8	47.41	60.49	70.82	74.39	76.71	78.78	80.58	81.96	d
•CF=O	-171.5	248.4	38.99	45.06	50.63	52.76	54.14	55.44	56.57	57.45	d
CF <sub>3</sub> O•	-655.6	275.2	56.44	73.91	86.83	90.89	93.40	95.56	97.32	98.66	h,e

References for Tables 1-3							
a	Kee et al. (1987)	i	Chen et al. (1975)				
b	Kolesov (1978)	j	this work, see text				
c	McMillen and Golden (1982)	k	Lacher and Skinner (1968)				
d	Stull and Prophet (1971)	l	Chen et al. (1990, 1991)				
e	Zachariah et al. (1995)	m	Daubert and Danner (1985)				
f	Pritchard et al. (1984)	n	Stadelman and Vogt (1980)				
g	Rodgers (1978)	o	Stull et al. (1969)				
h	Batt and Walsh (1982)	p	Gurvich et al. (1991)				

TABLE 3. Enthalpy of Formation, Entropy, Heat Capacities for C<sub>2</sub> Fluorocarbons

SPECIES	$\Delta H^\circ_f(298)$ kJ/mol	$S^\circ(298)$ J/mol/K	$C_p^\circ(T)$ J/mol/K								Ref
			300	500	800	1000	1200	1500	2000	3000	
CH <sub>3</sub> -CH <sub>2</sub> F	-263.2	265.0	59.83	87.22	116.47	129.62	139.71	150.28	159.35	164.18	i
CH <sub>2</sub> F-CH <sub>2</sub> F	-433.9	288.2	67.88	95.13	124.30	136.74	145.96	155.31	162.30	163.96	j,e
CH <sub>3</sub> -CHF <sub>2</sub>	-500.8	282.5	68.72	97.11	124.65	136.47	145.39	154.49	161.85	165.39	i
CH <sub>2</sub> F-CHF <sub>2</sub>	-664.8	311.7	75.31	107.53	133.47	143.93	151.98	159.92	169.26	177.71	k,e
CH <sub>3</sub> -CF <sub>3</sub>	-745.6	287.4	78.81	108.32	133.82	144.08	151.47	158.99	165.10	167.67	i
CHF <sub>2</sub> -CHF <sub>2</sub>	-877.8	314.8	85.23	115.25	141.25	150.60	156.64	163.29	169.67	173.93	j,e
CH <sub>2</sub> F-CF <sub>3</sub>	-895.8	316.2	86.58	118.04	143.15	152.09	158.17	164.43	169.66	171.50	i
CHF <sub>2</sub> -CF <sub>3</sub>	-1104.6	333.8	96.09	127.53	151.13	158.85	164.06	168.60	170.64	169.74	i
CF <sub>3</sub> -CF <sub>3</sub>	-1342.6	332.1	106.79	139.13	160.34	166.68	169.89	172.97	175.77	177.09	i
CH <sub>2</sub> F-CH <sub>2</sub> •	-44.6	279.8	58.13	80.27	103.74	114.31	122.42	130.91	138.24	142.37	1
CH <sub>3</sub> -CHF <sub>2</sub> •	-76.3	274.0	58.79	79.75	103.33	114.06	122.34	130.91	138.07	141.89	j,l
CH <sub>2</sub> F-CHF <sub>2</sub> •	-238.5	293.4	69.59	91.24	111.69	119.75	125.52	131.33	136.07	139.86	j,l
CHF <sub>2</sub> -CH <sub>2</sub> •	-277.2	297.8	67.06	90.20	111.94	121.10	128.00	135.04	140.63	142.60	1
CH <sub>3</sub> -CF <sub>2</sub> •	-302.5	290.4	67.34	89.22	111.30	120.80	127.83	135.52	142.85	147.42	g,l
CH <sub>2</sub> F-CF <sub>2</sub> •	-446.0	311.1	74.07	97.38	118.86	127.24	133.22	139.11	143.42	144.90	1
CHF <sub>2</sub> -CHF <sub>2</sub> •	-451.9	310.7	76.14	99.54	119.95	127.91	133.70	139.35	143.30	143.80	1
CF <sub>3</sub> -CH <sub>2</sub> •	-517.1	302.6	77.37	101.75	121.27	128.88	134.26	139.75	145.42	149.64	g,l
CHF <sub>2</sub> -CF <sub>2</sub> •	-664.8	328.4	84.32	107.31	127.04	134.10	138.83	143.26	145.92	145.88	j,l
CF <sub>3</sub> -CHF <sub>2</sub> •	-680.7	326.3	85.84	109.68	128.34	135.01	139.45	143.76	147.55	149.47	j,l
CF <sub>3</sub> -CF <sub>2</sub> •	-891.2	340.5	92.84	118.29	136.19	141.80	145.18	148.11	150.50	151.09	g,l
CH <sub>2</sub> =CHF	-140.1	262.3	50.61	71.66	91.80	100.57	107.42	114.10	118.92	121.04	p,m
CHF=CHF [Z]	-297.1	268.6	58.06	79.62	99.16	107.13	112.47	118.31	124.29	128.86	n,e
CHF=CHF [E]	-292.9	267.8	59.82	80.44	99.61	107.53	112.83	118.70	124.91	129.77	n,e
CH <sub>2</sub> =CF <sub>2</sub>	-336.4	265.2	59.33	81.55	100.20	107.74	113.14	118.70	123.44	125.80	p,o
CHF=CF <sub>2</sub>	-491.0	292.7	69.45	90.32	107.48	113.93	118.67	124.16	130.07	134.34	p,o
CF <sub>2</sub> =CF <sub>2</sub>	-658.5	299.9	80.70	100.40	115.53	120.89	123.89	126.87	129.64	131.27	d
CHF=CH <sub>2</sub> • [E]	124.3	258.0	50.61	67.10	81.56	87.66	92.21	97.15	101.75	104.49	e
CHF=CH <sub>2</sub> • [Z]	123.0	257.0	50.74	67.33	81.76	87.92	92.44	97.29	101.69	104.19	e
CH <sub>2</sub> =CF <sub>2</sub> •	109.2	256.8	50.22	66.10	80.71	86.89	91.30	96.37	101.64	105.58	e
CHF=CF <sub>2</sub> • [E]	-41.0	279.3	59.30	74.51	87.79	92.80	96.05	99.66	103.21	105.68	e
CHF=CF <sub>2</sub> • [Z]	-42.7	279.3	59.30	74.51	87.79	92.80	96.05	99.66	103.21	105.68	e
CF <sub>2</sub> =CH <sub>2</sub> •	-67.8	277.0	59.20	76.36	89.73	94.73	97.78	100.81	103.08	103.88	e
CF <sub>2</sub> =CF <sub>2</sub> •	-216.3	300.5	68.26	83.42	95.36	99.41	101.77	104.39	106.90	108.21	e
C <sub>2</sub> HF	125.5	231.5	52.48	62.17	69.69	73.22	75.83	78.82	81.96	84.57	d
C <sub>2</sub> F <sub>2</sub>	20.9	244.0	57.07	67.96	76.67	79.74	81.54	83.46	85.20	86.16	d
CHF=C=O	-147.2	270.5	56.75	71.49	84.93	90.34	94.31	98.24	101.99	102.12	e
CF <sub>2</sub> =C=O	-290.4	288.8	68.30	81.79	92.56	96.66	99.61	102.48	104.72	106.77	e
•CF=C=O	69.0	276.2	56.80	65.85	73.77	76.59	94.38	98.22	101.97	103.19	e

**Table 4. C<sub>1</sub> and C<sub>2</sub> Fluorinated Hydrocarbon Heats of Formation:  
Calculated Values (BAC-MP4), Literature Values, and Uncertainties**

SPECIES	BAC	Lit	Uncert	Ref	Lit	Ref	SPECIES	BAC	Lit	Uncert	Ref	Lit	Ref
CH <sub>4</sub>	-74.8	-74.9	0.4	a			C <sub>2</sub> H <sub>5</sub> •	120.6	118.5		a		
CH <sub>3</sub> F	-233.8	-232.6	8.4	b	-247.3	y	CH <sub>2</sub> F-CH <sub>2</sub> •	-56.2	-47.7	1.9	m	-44.6	z
CH <sub>2</sub> F <sub>2</sub>	-451.1	-452.2	1.8	b	-460.7	y	CH <sub>3</sub> -CHF•	-75.6	-76.3	5.9	m	-72.4	z
CHF <sub>3</sub>	-699.5	-697.6	4.2	b	-697.9	y	CH <sub>2</sub> F-CHF•	-247.3	-238.5	12.5	m	-235.5	z
CF <sub>4</sub>	-934.1	-933.0	0.4	b	-934.3	y	CHF <sub>2</sub> -CH <sub>2</sub> •	-280.9	-285.8	15.0	m	-277.2	z
•CH <sub>3</sub>	146.0	145.7	1.3	a			CH <sub>3</sub> -CF <sub>2</sub> •	-300.2	-302.5	8.4	o		
•CH <sub>2</sub> F	-31.4	-32.6	8.4	c			CH <sub>2</sub> F-CF <sub>2</sub> •	-460.1	-449.8	15.0	m	-446.0	z
•CHF <sub>2</sub>	-247.3	-247.7	8.4	c	-252.0	aa	CHF <sub>2</sub> -CHF•	-459.8	-456.1	15.0	m	-451.9	z
•CF <sub>3</sub>	-471.9	-467.4	8.4	c	-472.0	aa	CF <sub>3</sub> -CH <sub>2</sub> •	-526.6	-517.1	4.2	o		
:CH <sub>2</sub>	429.8	424.7	4.2	d			CHF <sub>2</sub> -CF <sub>2</sub> •	-671.1	-660.7	18.7	m	-660.2	z
:CHF	131.7	163.2	12.6	e	105.0	aa	CF <sub>3</sub> -CHF•	-703.0	-680.7	9.6	p	-688.3	z
:CF <sub>2</sub>	-203.3	-186.6	6.3	f	-180.0	aa	CF <sub>3</sub> -CF <sub>2</sub> •	-907.6	-891.2	4.2	o	-896.0	aa
•CH	613.7	594.1	0.4	g									
•CF	236.3	242.1	10.0	aa	255.2	g							
CH <sub>2</sub> =O	-108.5	-108.6	6.3	h									
CHF=O	-382.3	-376.6	15.0	g									
CF <sub>2</sub> =O	-598.4	-638.9	1.7	g	-640.0	aa							
•CH=O	38.9	37.2	8.4	a									
•CF=O	-182.9	-175.7	15.0	g	-179.0	aa							
CH <sub>3</sub> OH	-204.8	-201.2	0.4	a									
CF <sub>3</sub> OH	-919.4	-893.3	12.6	i									
CH <sub>3</sub> OF	-92.0	-72.4	12.6	i									
CF <sub>3</sub> OF	-750.1	-764.8	12.6	a									
CH <sub>3</sub> O•	27.6	16.7	2.9	j									
CF <sub>3</sub> O•	-628.3	-655.6	6.3	i									
CH <sub>3</sub> OOH	-124.6	-131.0	8.4	h									
CF <sub>3</sub> OOH	-807.5	-803.3	15.0	m									
CH <sub>3</sub> OO•	25.3	28.0	12.6	a									
CF <sub>3</sub> OO•	-627.5	-602.5	12.6	i									
HC(O)OH	-387.3	-378.6	0.4	h									
FC(O)OH	-614.9												
HC(O)O•	-124.9	-150.6	8.4	k									
FC(O)O•	-336.9												
C <sub>2</sub> H <sub>6</sub>	-86.9	-84.1	0.4	a									
CH <sub>3</sub> -CH <sub>2</sub> F	-272.4	-263.2	1.6	l									
CH <sub>2</sub> F-CH <sub>2</sub> F	-446.0	-433.9	11.8	m									
CH <sub>3</sub> -CHF <sub>2</sub>	-505.3	-500.8	6.3	l	-497.0	q							
CH <sub>2</sub> F-CHF <sub>2</sub>	-671.5	-664.8	4.2	n	-691.0	q							
CH <sub>3</sub> -CF <sub>3</sub>	-755.4	-745.6	1.6	l	-747.3	q							
CHF <sub>2</sub> -CHF <sub>2</sub>	-883.3	-877.8	17.6	m									
CH <sub>2</sub> F-CF <sub>3</sub>	-913.3	-895.8	4.2	l									
CHF <sub>2</sub> -CF <sub>3</sub>	-1124.1	-1104.6	4.6	l									
CF <sub>3</sub> -CF <sub>3</sub>	-1357.0	-1342.7	6.3	l	-1344.0	q							

**Table 4. C<sub>1</sub> and C<sub>2</sub> Fluorinated Hydrocarbon Heats of Formation:  
Calculated Values (BAC-MP4), Literature Values, and Uncertainties**

a Tsang and Hampson (1986)	q Kolesov and Papina (1970)
b Kolesov (1978)	r Stadelmann and Vogt (1980)
c McMillen and Golden (1982)	s Stull et al. (1969)
d Kee et al (1987)	t Bryant (1962)
e Pritchard et al (1984)	u Nuttall et al. (1971)
f Rodgers (1978)	v Lias et al. (1988)
g Stull and Prophet (1971)	w Kerr and Timlin (1971)
h Baulch et al (1984)	x Tschuikow-Roux and Salomon (1987)
i Batt and Walsh (1982)	y Rodgers et al. (1974)
j Batt et al (1974)	z Chen et al. (1990, 1991)
k Benson (1976)	aa Gurvich et al (1991)
l Chen et al. (1975)	
m this work, see text	H <sub>f</sub> (298)      Calculated Heat of Formation at 298 K
n Lacher and Skinner (1968)	Lit      Literature Value for H <sub>f</sub> (298)
o Rodgers (1978)	Uncert      Reported Uncertainty in Literature Value
p Martin and Paraskevopoulos (1983)	Ref      Literature Reference



### 3. Reaction Kinetics

#### 3.1. Overview

The reaction set or "mechanism" is too large to be described in detail here and, consequently, only an overview of important classes of reactions will be presented. Utilizing the species identified as potentially important, a grid of possible reactions was constructed. Existing chemical rate data involving these fluorinated species was then compiled and evaluated. Where rate data were available, but only over limited temperature ranges or at different pressures (for unimolecular or chemically activated steps), RRKM (Robinson and Holbrook, 1972) and QRRK (Dean and Westmoreland, 1987) methods were used to estimate the temperature dependencies (at 1 atmosphere) of the rates and to predict relative rates where multiple product channels were possible. Where no rate data were available for potential reactions, the rate constants were estimated by analogy to other hydrocarbon or substituted hydrocarbon reactions. The prefactors were adjusted for reaction path degeneracy and the activation energies were adjusted empirically based on relative heats of reaction or relative bond energies (*i.e.*, Evans-Polanyi relationships).

Initially, upper limits were used for estimated rate constants. If as a result of simulations under a variety of conditions (using different agents, flame geometries, etc.), it was observed that a specific reaction with an upper limit rate constant did not significantly contribute to the destruction or creation of any of the species in the "mechanism," then that estimate was continued to be used. However, if a specific reaction contributed to the chemistry and its rate constant was an upper-limit estimate, then its value was re-examined and possibly refined. For important contributing reactions where no good analogy was available, where significant uncertainty existed in the barrier (generally reactions with tight transition states and modest-to-large barriers), or where multiple, energetically similar product channels were possible, we calculated the geometries and energies of the transition states (Zachariah *et al.*, 1995) using the BAC-MP4 *ab initio* method. RRKM methods were then applied to obtain the temperature (and pressure) dependence of the rate constant.

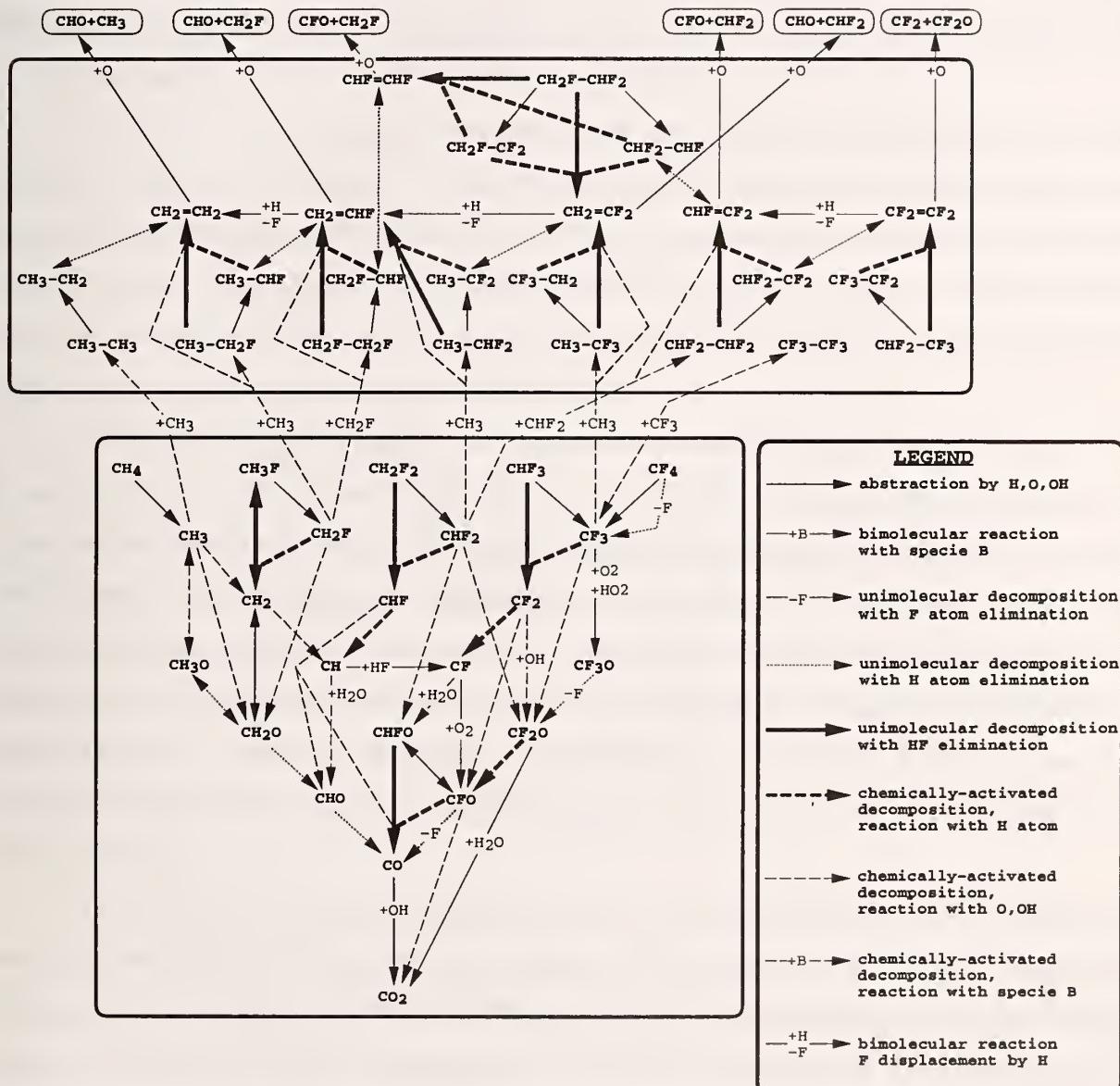
A listing of the rate constants in the reaction set or mechanism used in the simulations is given below in Table 5. In addition, other reactions were also considered but were observed not to contribute under the conditions tested. Many of the relevant rate constants can be found in the "NIST Chemical Kinetics Database" (Mallard *et al.*, 1993).

A qualitative discussion of the uncertainties in the rate expressions is provided with each class of reaction. For rate expressions traceable to experimental measurements, quantitative evaluation of the uncertainties can be found in the original sources.

A schematic of the possible reaction pathways for the fluorinated hydrocarbon mechanism is given in Figure 1. This schematic provides no indication of the relative contributions of each of the possible reaction pathways since this is highly dependent upon conditions. Rather, this schematic gives an indication of the connectivity between all of the species and how the different types of reaction (*e.g.*, thermal decompositions, chemically activated decompositions, abstractions, etc.) provide this connectivity between different types of species. For example, the linkages between each fluoromethane and the corresponding fluoromethylene is due to thermal decomposition and are indicated with bold solid arrows. Other thermal decompositions involving HF elimination (*e.g.*, fluoroethanes  $\rightarrow$  fluoroethylenes,  $\text{CHF}=\text{O} \rightarrow \text{CO}$ ) are also represented by bold solid arrows. Thermal decompositions involving H and F atom elimination are represented by plain dotted arrows. H atom addition/elimination reactions are represented by reversible plain dotted arrows (*e.g.*,  $\text{CH}_3\text{-CHF}\cdot \leftrightarrow \text{CH}_2=\text{CHF} + \text{H}$ ). Similarly, chemically activated decompositions, such as fluoromethyls  $\rightarrow$  ["hot" fluoromethanes]  $\rightarrow$  fluoromethylene, are represented by bold dashed arrows (for reactions involving H atoms) and plain dashed arrows (for reactions involving O atoms and OH radicals). Abstraction type reactions (*e.g.*, fluoromethanes  $\rightarrow$  fluoromethyls) are represented by plain solid arrows. A few of the potential reaction pathways are not shown in Figure 1 for purposes of maintaining clarity in the schematic representation.

For any given condition (*e.g.*, temperature, concentration) and any given fluorocarbon, only a subset of the reactions pathways will be relevant. For each reaction pathway that is possible, each will have a different relative importance. A discussion of each of the different reaction types for each species type can be found in the following sections.

**Figure 1. Fluorinated Hydrocarbon Reaction Pathways**





### 3.2. Hydrocarbon and H/O/F Chemistry

The C/H/O subset is derived from the Miller-Bowman mechanism (Miller and Bowman, 1989) and consists of about 30 species and 140 reactions (see reactions HO-xx, HC-xx in Table 5). Any other hydrocarbon mechanism could be used instead. For example, the GRIMECH set (Bowman *et al.*, 1995) is a new hydrocarbon mechanism that accurately reproduces flame speeds for methane mixtures.

The H/O/F subset consists of 3 species (F, HF) and 8 reactions (reactions HF-xx in Table 5) that are relatively well known. This is the chemistry of fluorine atoms with hydrogen- and oxygen-containing species, such as H<sub>2</sub>, OH, and H<sub>2</sub>O. There are three reactions of this type that were determined to participate in the chemistry under a variety of conditions. These reactions are the combination of H and F to form HF (and the reverse decomposition) and the hydrogen atom transfer reactions by F atoms from H<sub>2</sub> and H<sub>2</sub>O.

The HF decomposition reaction has been measured only at temperatures above about 4000 K (Jacobs *et al.*, 1965; Blauer, 1968, Blauer *et al.*, 1971). Although this reaction in the decomposition direction is unimportant at typical flame temperatures, the reverse H + F = HF combination must be considered. Extrapolating the recommended value (Baulch *et al.*, 1981) for decomposition to 1000 K may result in an uncertainty of as much as a factor of ten, especially when considering non-simple Arrhenius dependence to the rate and different third-body efficiencies. However, since many other reactions (F + H<sub>2</sub>, H<sub>2</sub>O, RH) contribute to F atom destruction, the uncertainty in the absolute rate of the forward or reverse reaction is most likely unimportant.

The hydrogen abstraction reactions of F atoms with H<sub>2</sub> and H<sub>2</sub>O have been measured only near room temperature (Wurzberg and Houston, 1980; Stevens *et al.*, 1989; Walther and Wagner, 1983). These values were extended to higher temperatures by fitting the reported values to extended Arrhenius expressions. For the H<sub>2</sub> reaction, an expression with T<sup>0.5</sup> dependence was chosen consistent with the value recommended by Cohen and Westberg (1983). For the H<sub>2</sub>O reaction, an expression with T<sup>1.5</sup> dependence was chosen by analogy to other reactions.

There are a number of other reactions which were included in the mechanism, but were never observed to contribute significantly to the chemistry. These reactions include the combination of F atoms to form  $F_2$  and the hydrogen abstractions by F atoms from OH, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>. The oxy-fluoro-species FO•, HO<sub>2</sub>F, FOO•, and F<sub>2</sub>O were also initially considered in the mechanism. However, given the very low concentration of F atoms at high temperatures in the hydrocarbon/air flame, these species are present in extremely low concentrations and do not contribute to the overall chemistry. The rate constants used for reactions involving these species will be detailed later in another publication.

### 3.3. C<sub>1</sub> Fluorinated Hydrocarbon Chemistry

#### 3.3.1. Overview

The C<sub>1</sub> subset of the reaction set (approximately 150 reactions) consists of chemistry of 14 species containing one carbon (and hydrogen/fluorine/oxygen) with H, O, OH, H<sub>2</sub>O, and other flame species (see reactions MD-xx, MA-xx, NN-xx, PP-xx, CF-xx in Table 5). The C<sub>1</sub>/H/F/O species used in this reaction set are the fluoromethanes (CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub>, CF<sub>4</sub>), the fluoromethyl radicals (•CH<sub>2</sub>F, •CHF<sub>2</sub>, •CF<sub>3</sub>), the fluoromethylenes (:CHF, :CF<sub>2</sub>), and the fluoromethylidyne radical (•CF). The oxidized C<sub>1</sub> fluorocarbon species contained in this reaction set are the perfluoromethoxy radical (CF<sub>3</sub>O•) and the carbonyl fluorides (CHF=O, CF<sub>2</sub>=O, •CF=O). Other oxidized C<sub>1</sub> fluorocarbon species were initially considered in the development of the mechanism, but later were excluded, as were the other fluoromethoxy radicals (CH<sub>2</sub>FO•, CHF<sub>2</sub>O•), the fluorohydroxymethyl radicals (•CHFOH, •CF<sub>2</sub>OH), the perfluoromethylperoxy radical (CF<sub>3</sub>OO•), and perfluoromethanol (CF<sub>3</sub>OH). Although these species (and others) may be important in atmospheric chemistry, our initial simulations suggest that they are present in extremely low concentrations at high temperatures in hydrocarbon/air flames and do not contribute to the overall chemistry.

Both thermally and chemically activated decompositions are considered (*e.g.*, CH<sub>2</sub>F<sub>2</sub> → :CHF + HF and •CHF<sub>2</sub> + H → :CHF + HF). Fluoromethane decompositions via abstraction of H atoms by H, O, and OH radicals are important pathways. Fluoromethane metathesis reactions with methyl, ethyl, vinyl, and fluoromethyl radicals are also considered. The reaction set also includes reactions of fluoromethyls with O<sub>2</sub>, O, and OH to form carbonyl fluorides (*e.g.*, CF<sub>2</sub>=O) and other products, and reactions of the fluoromethylenes (*e.g.*, :CF<sub>2</sub>) with H to form •CF and O<sub>2</sub>, O, or OH to form carbonyl fluorides. The carbonyl fluorides (*i.e.*, CHF=O, CF<sub>2</sub>=O, and •CF=O) can be destroyed via unimolecular decomposition, by reactions with H atoms (both abstractions and addition/eliminations), and through reactions with OH radicals (abstractions). Destruction of CF<sub>2</sub>=O through complex formation with H<sub>2</sub>O and subsequent decompositions are also considered.

### 3.3.2. Fluoromethanes: Decompositions

The fluoromethanes are primarily destroyed in hydrocarbon flames by H atom abstraction by H and OH and through unimolecular decomposition. Destruction by H atom abstraction by O atoms is a minor channel. The biggest uncertainties for the destruction of the fluoromethanes are the unimolecular decompositions. Although there are good quality experimental data for these reactions, their strong temperature and pressure dependence results in a level of uncertainty to these reactions at flame temperatures. Further mechanism refinements should provide better rate expressions for these reactions.

Both thermally and chemically activated decompositions of the fluoromethanes were considered (*e.g.*,  $\text{CHF}_3 \rightarrow :CF_2 + HF$  and  $\cdot\text{CHF}_2 + H \rightarrow :CF_2 + HF$ ). There have been a number of measurements of the unimolecular decomposition of fluoromethanes (with HF elimination). We employed rate expressions for HF elimination from  $\text{CH}_3\text{F}$  and  $\text{CHF}_3$  that are fits using an extended Arrhenius form to the experimental data of Schug and Wagner (1973) and Hidaka *et al.* (1991), respectively. These experimental data were obtained at different temperatures and pressures than are relevant to atmospheric flames. The experimental data were interpolated or extrapolated and fit using temperature dependencies ( $T^b$ ) that were consistent with the experimental data and our RRKM calculations. For HF elimination from  $\text{CH}_2\text{F}_2$ , we employed a rate expression from our BAC-MP4/RRKM calculations, although there is reasonable experimental data by Politanskii and Shevchuk (1968). For  $\text{H}_2$  elimination (minor channel) from  $\text{CH}_3\text{F}$  and  $\text{CH}_2\text{F}_2$ , we used rate expressions from our RRKM calculations using our BAC-MP4 *ab initio* barriers (Zachariah *et al.*, 1995). F atom eliminations from the fluoromethanes are negligible decomposition channels, except for  $\text{CF}_4$ , where it is the only possible pathway. For this reaction, we used a rate expression from our RRKM calculations that is based on the room-temperature measurement of the reverse reaction ( $\cdot\text{CF}_3 + F$ ) by Plumb and Ryan (1986).

There have been no measurements (to our knowledge) for reactions involving chemically activated or "hot" fluoromethanes other than room temperature measurements of the rate constant for  $\text{CF}_3 + H \rightarrow \text{Products}$  (*e.g.*, Ryan and Plumb, 1984; Tsai and McFadden, 1989). In order to estimate values for these various reactions, as well as for the stabilized fluoromethane

channels, we used RRKM methods with experimental (where they existed) or our BAC-MP4 *ab initio* barriers (Zachariah *et al.*, 1995) for insertion of :CHF and :CF<sub>2</sub> into HF and H<sub>2</sub> and the energetics of the reaction pathways. Although there are no experimental rate measurements at flame temperatures for chemically activated fluoromethane decompositions and these are primary pathways for destruction of fluoromethyl radicals, the corresponding uncertainties in the rates are small, since these are barrierless combinations.

There have been a number of measurements of the unimolecular decomposition of fluoromethanes (with HF elimination): at least two for CH<sub>3</sub>F (Politanskii and Shevchuk, 1967; Schug and Wagner, 1973), at least one for CH<sub>2</sub>F<sub>2</sub> (Politanskii and Shevchuk, 1968), and several for CHF<sub>3</sub> (Tschuikow-Roux, 1965; Tschuikow-Roux and Marte, 1965; Modica and LaGraff, 1966; Politanskii and Shevchuk, 1968; Biordi *et al.*, 1978; Schug *et al.*, 1979; Hidaka *et al.*, 1991). In addition, there have been quite a few measurements of the unimolecular decomposition of other halomethanes (eliminating HF, HCl, or HBr) such as CHF<sub>2</sub>Cl (Norton, 1957; Edwards and Small, 1964; Gozzo and Patrick, 1964; Edwards and Small, 1965; Gozzo and Patrick, 1966; Barnes *et al.*, 1971; Kushina *et al.*, 1972; Schug *et al.*, 1979; Zhitnev *et al.*, 1990; Zhitnev *et al.*, 1991), CHF<sub>2</sub>Br (Cox and Simmons, 1971), CHFCl<sub>2</sub> (Kushina *et al.*, 1972), and CHCl<sub>3</sub> (Shilov and Sabirova, 1960; Schug *et al.*, 1979). All of these halomethane decomposition reactions have a small-to-moderate barrier in the reverse direction (*i.e.*, carbene insertion into HF, HCl, or HBr) of 10-40 kJ/mol. Consequently, all of the halomethane measurements are important from the point of evaluating the fluoromethane values (both experimental and calculated) for consistency. Furthermore, the barriers-to-insertion for :CHF and :CF<sub>2</sub> in these reactions can be used as reference reactions for reactions of :CHF and :CF<sub>2</sub> with many other important molecules where there is no or little information available (*i.e.*, the reactions of :CHF and :CF<sub>2</sub> with H<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, fluoromethanes, fluoromethyls, etc.).

### 3.3.3. Fluoromethanes: H Abstractions by H Atoms

In this work, we have used our fits to extended Arrhenius form to the experimental data of Westenberg and deHaas (1975), Ridley *et al.* (1972), and Arthur and Bell (1978) for H atom abstraction from CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, and CHF<sub>3</sub>, respectively. A temperature dependence of T<sup>3.0</sup> was used in analogy to the recommended value (Tsang and Hampson, 1986) for H atom abstraction from methane (CH<sub>4</sub>). The experimental data were all obtained at modest temperatures (600 K–900 K) and, consequently, the uncertainties in extrapolation of these data to flame decomposition temperatures are most likely acceptable. We note that based on our limited evaluation (Burgess *et al.*, 1994), the trends in the rate expressions for this homologous series appear to be consistent with the number of H atoms in the molecules and the C-H bond strengths (or heats of reaction).

There have been quite a number of measurements for H atom abstractions from fluoromethanes by H radicals, but only a few for H atom abstraction by O or OH radicals. For H atom abstraction by H radicals, there have been at least four measurements for CH<sub>3</sub>F (Parsamyan *et al.*, 1967; Hart *et al.*, 1974; Westenberg and deHaas, 1975; Aders *et al.*, 1975), at least two measurements for CH<sub>2</sub>F<sub>2</sub> (Parsamyan and Nalbandyan, 1968; Ridley *et al.*, 1972), and quite a few for CHF<sub>3</sub> (Ayscough and Polanyi, 1956; Pritchard *et al.*, 1956; Skinner and Ringrose, 1965; Amphlett and Whittle, 1967; Arthur and Bell, 1968; Fagarash and Moin, 1968, Kibby and Weston, 1968; Berces *et al.*, 1972; Kondratiev, 1972; Arthur *et al.*, 1975; Arthur and Bell, 1978; Richter *et al.*, 1994). We should note that many of the measurements for the CHF<sub>3</sub> reactions are actually measurements of the reverse rate or •CF<sub>3</sub> + H<sub>2</sub> → CHF<sub>3</sub> + H. Two of the citations (Kondratiev, 1972; Arthur and Bell, 1978) are evaluations of the experimental data. We have also calculated (Zachariah *et al.*, 1995) the structure and energy of each transition state for these H atom abstraction reactions from the fluoromethanes using the BAC-MP4 *ab initio* method. The calculated energy barriers compare well with the experimental values.

For the CH<sub>3</sub>F + H reaction, all of the workers cited above incorrectly identified the reaction as abstraction of F atoms rather than H atoms. These workers only measured the disappearance of the reactants and simply assigned the product channel by analogy to the CH<sub>3</sub>Br

+ H reaction, where it is known that the halogen atom (Br) is abstracted. However, the C-F bond is much stronger than the C-Br bond or even the C-H bond. Consequently, in CH<sub>3</sub>F, the H atom, rather than the F atom, is abstracted. Our *ab initio* calculations (Zachariah *et al.*, 1995) also support this argument, where H atom abstractions from the fluoromethanes by H atoms were calculated to have energy barriers of 49.4, 40.6, 53.6 kJ/mol for the CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub> series, respectively. These same calculations yield barriers-to-abstraction of F atoms of 131.4, 142.7, 168.6, 171.1 kJ/mol for the CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub>, CF<sub>4</sub> series, respectively. This is a significant difference and clearly supports assignment of H atom abstraction as the dominant channel.

Richter *et al.* (1994) have recently measured the rate of H atom abstraction from CHF<sub>3</sub> by H in H<sub>2</sub>/O<sub>2</sub> premixed flames and report an activation energy of about 73 kJ/mol. This barrier would appear to be inconsistent with and significantly higher than typical values of 40-50 kJ/mol for H atom abstraction by H from hydrocarbons (*e.g.*, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) and other fluoromethanes (see references above).

### 3.3.4. Fluoromethanes: H Abstractions by O Atoms and OH Radicals

In this work, for H atom abstraction by O atoms, we fit experimental data for CH<sub>3</sub>F (Parsamyan *et al.*, 1967), CH<sub>2</sub>F<sub>2</sub> (Parsamyan and Nalbandyan, 1968), and CHF<sub>3</sub> (Jourdain *et al.*, 1978) using an extended Arrhenius expression with a temperature dependence (T<sup>1.5</sup>) by analogy to methane (Tsang and Hampson, 1986). For H atom abstraction by OH radicals, we used rate expressions recommended by Cohen and Benson (1987a, 1987b) that have temperature dependencies based on transition state theory. These recommendations are based on experimental measurements at relatively low temperatures (about 300 K-500 K). Since these reactions are primary decomposition pathways for the fluoromethanes, it would be valuable to have experimental measurements of these rates at higher temperatures (closer to flame conditions). We note that based on our limited evaluation, the trends in the rate expressions for these homologous series (both O and OH) appear to be consistent with changes in the number of H atoms and the C-H bond strengths or heats of reaction.

There have been quite a number of measurements for H atom abstractions from fluoromethanes by H radicals, but only a few for H atom abstraction by O or OH radicals. Parsamyan and coworkers have measured the rate of reaction for CH<sub>3</sub>F + O (Parsamyan *et al.*, 1967) and for CH<sub>2</sub>F<sub>2</sub> + O (Parsamyan and Nalbandyan, 1968). Jourdain *et al.* (1978) and Miyoshi *et al.* (1993) have measured the rate of reaction for CHF<sub>3</sub> + O. We have not used the more recent value by Miyoshi *et al.* (1993), because it appears that these data may be complicated by the CHF<sub>3</sub> → :CF<sub>2</sub> + HF decomposition reaction at the highest temperatures. This should be examined in more detail, since our conclusion was based on a limited evaluation of the data. Richter *et al.* (1994) have recently measured the rate of H atom abstraction from CHF<sub>3</sub> by O in H<sub>2</sub>/O<sub>2</sub> premixed flames and report an activation energy of about 13 kJ/mol. This barrier would appear to be inconsistent with and significantly lower than typical values of 35-40 kJ/mol for H atom abstraction by O from hydrocarbons (*e.g.*, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) and other fluoromethanes (see references above).

As indicated above, Cohen and Benson (1987a, 1987b) used transition-state theory calculations to analyze and predict rate coefficients for reaction of OH radicals in a series of halogen-substituted methanes and ethanes. Much of their analysis is based on the experimental

data of Jeong and Kaufman (1982), but it is also consistent with other measurements for fluoromethanes (Howard and Evenson, 1976; Clyne and Holt, 1979; Nip *et al.*, 1979; Talukdar *et al.*, 1991).

### 3.3.5. Fluoromethanes: H Abstractions by F and F Abstractions by H

There have been a number of measurements of H atom abstraction from methane ( $\text{CH}_4$ ) by F atoms near room temperature (Wagner *et al.*, 1971; Pollock and Jones, 1973; Williams and Rowland, 1973; Manning *et al.*, 1975; Smith *et al.*, 1977; Clyne and Hodgson, 1983; Pagsberg *et al.*, 1988). In our work, we used a fit to extended Arrhenius form to the rate constant of recommended by Atkinson *et al.* (1992) using a reasonable temperature dependence ( $T^{0.5}$ ) in order to extend the rate expression to flame temperatures. Although there is some uncertainty here in extrapolating the rate constant to flame temperatures, it is most likely unimportant. This is because this reaction occurs on almost every collision (that is, the rate cannot change by much). Furthermore, there are many other reactions (*e.g.*, F + H<sub>2</sub>, F + H<sub>2</sub>O, and F + other hydrocarbons) that contribute to F atom destruction.

For completeness in the reaction set (although it is unlikely that they will contribute), we have also included H atom abstractions from the fluoromethanes by F atoms. There have been a number of measurements for these reactions near room temperature for CH<sub>3</sub>F (Pollock and Jones, 1973; Smith *et al.*, 1977; Manocha *et al.*, 1983), for CH<sub>2</sub>F<sub>2</sub> (Pollock and Jones, 1973; Smith *et al.*, 1977; Manocha *et al.*, 1983, Clyne and Hodgson, 1985; Nielsen *et al.*, 1992), and for CHF<sub>3</sub> (Pollock and Jones, 1973; Goldberg and Schneider, 1976; Smith *et al.*, 1977; Clyne and Hodgson, 1983; Maricq and Szente, 1992). For these reactions, rate expressions were used where the rate constant prefactor relative to that recommended by Atkinson *et al.*, 1992) for CH<sub>4</sub> + F was adjusted to account for reaction path degeneracy (*i.e.*, fewer number of H atoms) and the activation energy was adjusted such that the rate was consistent with the measurements at room temperature. Use of extended Arrhenius form in these cases is not justified, because of the lack of temperature-dependent experimental measurements.

For F atom abstractions from CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, and CHF<sub>3</sub> by H radicals, we employed rate expressions derived from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995). The F atom abstraction pathways are negligible channels and these reactions were included simply for completeness in development of this reaction set. However, for reaction of H atoms with CF<sub>4</sub>, the only possible pathway is F atom abstraction. For this reaction, we have used the experimentally derived rate expression of Kochubei and Moin (1969, 1971). This reaction is

very important pathway for  $\text{CF}_4$  destruction, competing with the only other possible channel - unimolecular decomposition of  $\text{CF}_4$  to  $\bullet\text{CF}_3$  and F.

### 3.3.6. Fluoromethanes: Metathetical Reactions

There have been quite a few measurements of metathetical reactions of methyl/fluoromethyl radicals with methane/fluoromethanes. These will not be reviewed here. In our work, we used the recommendations of Kerr and Parsonage (1976), which are consistent with the majority of the experimental data and empirical relationships for the barriers-to-reactions (activation energies). The values recommended by Kerr and Parsonage are largely based on the pioneering work in this area by Pritchard and coworkers (*e.g.*, Pritchard *et al.*, 1965), Whittle and coworkers (*e.g.*, Chamberlain and Whittle, 1972), and Arthur and coworkers (*e.g.*, Arthur and Bell, 1978). We note that based on our limited evaluation, the trends in the preexponentials and activation energies in the rate expressions for this homologous series appear to be consistent with changes in the number of H atoms and the C-H bond strengths or heats of reaction, respectively.

Although there have been no experimental measurements of metathetical reactions of vinyl radicals ( $C_2H_3$ ) with the fluoromethanes, one can estimate their rates by analogy to the methyl radical ( $CH_3$ ) reactions. We used rate expressions for these reactions, where the activation energy was reduced by 10%. This amount determined using the roughly 6 kJ/mol decrease in the heat of reaction and an empirical relationship we determined for a series of abstraction reactions (Burgess *et al.*, 1994).

Given the abundance of H and OH radicals in hydrocarbon flames and the somewhat higher barrier for H atom abstraction by methyl/fluoromethyl and vinyl radicals, these are secondary reaction pathways. However, under pyrolytic conditions they may contribute (especially the  $C_2H_3$  reactions which have the lowest barriers) and, consequently, for completeness should be retained in the reaction set. The experimental measurements for H atom abstractions by the methyl/fluoromethyl radicals were all made at relatively low temperatures (about 300 K-600 K). Extrapolation of these measurements to flame decomposition temperatures may introduce significant uncertainty in the rates, especially since these reactions should have considerable non-simple Arrhenius temperature dependencies. In further refinement of this mechanism, these data should be critically evaluated. Experimental measurements at significantly higher temperatures would also be extremely valuable.

### 3.3.7. Fluoromethyl Radical Destruction

Fluoromethyl radicals are destroyed by three general pathways whose relative importances are sensitive to conditions. 1) They can combine with H atoms forming chemically activated fluoromethanes that eliminate HF (creating methylene/fluoromethylenes). 2) They can react with oxygen-containing species (*i.e.*, O<sub>2</sub>, O, OH), resulting in the formation of fluoromethoxy radicals and carbonyl fluoride species. 3) They can combine with methyl or fluoromethyl radicals, forming chemically activated fluoroethanes that may be either stabilized or eliminate HF (creating ethylene/fluoroethylenes). This latter class of reactions is included with the fluoroethane (C<sub>2</sub>) chemistry.

The fluoromethyl radicals are primarily formed by H atom abstractions from the fluoromethanes. However, there are several other channels that can contribute to their formation and are classified as C<sub>2</sub> chemistry. For example, the reactions CH<sub>2</sub>=CHF + O → •CH<sub>2</sub>F + HCO and CHF<sub>2</sub>-CF<sub>2</sub>• + H → •CHF<sub>2</sub> + •CHF<sub>2</sub> contribute to the formation of fluoromethyl radicals. Similarly, there are a number of other decomposition channels that can be classified as C<sub>2</sub> or C<sub>3</sub> chemistry, such as •CH<sub>2</sub>F + C<sub>2</sub>H<sub>4</sub> → •CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>F.

There are four potential reaction product channels following association of fluoromethyl radicals (*e.g.*, •CHF<sub>2</sub>) with O<sub>2</sub> (by analogy to hydrocarbon and chlorinated hydrocarbon chemistry). 1) Stabilization of the fluoromethylperoxy radicals (*e.g.*, CHF<sub>2</sub>OO• product). 2) Internal abstraction of a hydrogen atom followed by O-O bond breakage (*e.g.*, CF<sub>2</sub>=O + OH products). 3) Internal abstraction of a fluorine atom followed by O-O bond breakage (*e.g.*, CHF=O + OF products). 4) Direct dissociation of the O-O bond (*e.g.*, CHF<sub>2</sub>O• + O products). The first channel (stabilization) should be negligible at flame temperatures, but may need to be considered at lower temperatures and for ignition delays. The second channel (H abstraction) should be a secondary pathway at flame temperatures, but clearly should be re-examined at lower temperatures. The third channel (F abstraction) can clearly be disregarded, because of the strong C-F bond. This contrasts to the analogous reactions that are assumed to occur in chlorinated hydrocarbon chemistry (*e.g.*, Ho *et al.*, 1992). Consequently, eliminating the first three potential pathways, we must only explicitly consider the fourth channel (direct O-

O bond dissociation) to form fluoromethoxy radicals and oxygen atoms (*e.g.*,  $\text{CHF}_2\text{O}\cdot + \text{O}$  products).

There have been a number of rate measurements for the reaction of  $\cdot\text{CF}_3$  with  $\text{O}_2$  near room temperature (Vedeneev *et al.*, 1978; Ryan and Plumb, 1982; Caralp *et al.*, 1986; Cooper *et al.*, 1988; Orlando and Smith, 1988), but none (to our knowledge) for reaction of the other fluoromethyl radicals with  $\text{O}_2$ . At low temperatures the only possible product pathway is formation of the fluoromethylperoxy radical. These types of radical species are known to play a role in atmospheric chemistry. At high temperatures in a flame, these species will be present in significantly smaller concentrations and there are other possible product pathways for the fluoromethyl +  $\text{O}_2$  reactions. For  $\cdot\text{CF}_3 + \text{O}_2 \rightarrow \text{CF}_3\text{O}\cdot + \text{O}$ , we estimated a rate expression from our RRKM calculations using the reasonable assumption that there is no barrier in the reverse direction. For the other two fluoromethyl reactions, we assumed the fluoromethoxy radical would be present in steady state concentrations and that they would rapidly eliminate HF after being formed. Based on these assumptions then, we simply used the  $\cdot\text{CF}_3$  rate expression after adjusting for reaction enthalpies. For lower temperature conditions (than flames), these assumptions and the relevant reaction pathways and rate expressions should be re-examined.

For reaction of the perfluoromethyl radical ( $\cdot\text{CF}_3$ ) with O atoms (eliminating F), we used a rate constant corresponding to the room temperature value measured by McFadden and coworkers (Tsai *et al.*, 1989). For reaction of the other fluoromethyl radicals with O atoms (eliminating H), we used rate constants scaled between that for  $\cdot\text{CH}_3$  and  $\cdot\text{CF}_3$ . For reaction of the fluoromethyl radicals with OH radicals, we used rate constants identical to that for  $\cdot\text{CH}_3$ .

Fluoromethyl radicals are primarily destroyed in hydrocarbon flames through reactions with H, OH, and  $\cdot\text{CH}_3$  radicals. Reactions with O atoms are minor channels. The biggest uncertainty here is likely the reactions with  $\cdot\text{CH}_3$  radicals (HF elimination versus stabilization), which are very temperature and pressure dependent. Further refinements of this mechanism should provide better rate expressions for these reactions, benchmarking them to experimental data that exists (see brief discussion in Fluoroethane Chemistry section).

Reaction of fluoromethyl radicals with  $\text{HO}_2$  may be important for correctly describing ignition delays. There are two possible product channels:  $\cdot\text{CHF}_2 + \text{HO}_2 \rightarrow \text{CH}_2\text{F}_2 + \text{O}_2$

(disproportionation and chain termination) versus  $\bullet\text{CHF}_2 + \text{HO}_2 \rightarrow \text{CHF}_2\text{O}\bullet + \text{OH}$  (combination/elimination and chain propagation). We estimated rate expression by analogy to the corresponding reaction. We assumed the fluoromethoxy radicals immediately eliminate an H atom, since the C-H bond strengths are only 25-30 kJ/mol. This eliminates the need for explicitly including these species in the mechanism. For the  $\text{CF}_3\text{O}\bullet$  product, a fast subsequent F atom elimination step (which is explicitly included in the reaction mechanism) does not happen immediately, since the C-F bond dissociation energy is about 110 kJ/mol. If these reactions (for  $\text{CH}_2\text{FO}\bullet$  and  $\text{CHF}_2\text{O}\bullet$ ) are shown to be important for ignition delays, then the rates and branching ratios should be re-examined.

### 3.3.8. Fluoromethylene Destruction

Estimates for the rates of reactions of the fluoromethylenes ( $:CHF$  and  $:CF_2$ ) with many species are somewhat uncertain, because reactions involving these species are significantly slower than the analogous reactions for singlet methylene ( $^1:CH_2$ ). There also appear to be conflicting experimental data on their reactivities. This will not be discussed here. The fluoromethylenes can be destroyed in a number of different ways.

- 1) They can be destroyed by reaction with H atoms, where we used rate expressions consistent with the room temperature values measured by McFadden and coworkers (Tsai and McFadden, 1989; Tsai and McFadden, 1990). For  $:CF_2 + H$  (which was slightly slower), this necessitates a small barrier (5 kJ/mol) to be used.
- 2) They can be destroyed by reaction with O atoms, where we used rate expressions consistent with the room temperature values measured by McFadden and coworkers (Tsai and McFadden, 1990). A small barrier (4 kJ/mol) for the  $:CF_2$  reaction was used.
- 3) They can be destroyed by reaction with OH radicals, where we used rate expressions consistent with the value for  $CF_2$ : determined by Biordi *et al.* (1978) in their flame measurements. Again a small barrier (14 kJ/mol) was used for  $:CF_2$  and no barrier for  $:CHF$ .
- 4) They can be destroyed by reaction with  $O_2$ , where we used the rate expression for  $:CF_2$  measured by Keating and Matula (1977). For  $:CHF$ , we used an equivalent rate expression (after adjusting for reaction enthalpy) with a significantly reduced, but still modest (24 kJ/mol) barrier. Since the  $:CHF$  reaction barrier has no experimental basis, if it is identified as a reaction that significantly contributes to the destruction of  $:CHF$ , then this reaction should be re-examined. An *ab initio* transition state calculation would be extremely useful in resolving this uncertainty.
- 5) They can be destroyed via insertion into  $H_2O$  (a major flame species). We estimated barriers to reaction of 25 and 100 kJ/mol for  $:CHF$  and  $:CF_2$ , respectively, from our BAC-MP4 *ab initio* calculations.
- 6) The fluoromethylenes can also be destroyed via reaction with hydrocarbons (see brief discussion in Fluoroethane Chemistry section).

The fluoromethylenes ( $:CHF$  and  $:CF_2$ ) are largely destroyed in hydrocarbon flames via reaction with H atoms. Reactions with O and OH radicals are minor channels. There are good quality experimental data for all of the reactions, which proceed with small barriers. An open question here is the probable addition of the fluoromethylenes to ethylene. This class of reactions has been ignored in this mechanism in order to minimize the number of species in the reaction set, because these reactions would lead to the formation of C<sub>3</sub> fluorinated hydrocarbons.

### 3.3.9. Fluoromethylidyne Destruction

The rates of reactions of fluoromethylidyne ( $\bullet\text{CF}$ ) with many species are somewhat uncertain given they are significantly slower than the analogous reactions for methylidyne ( $\bullet\text{CH}$ ). There also appear to be conflicting experimental data on its reactivity. This will not be discussed here. For the reactions of  $\bullet\text{CF}$  with  $\text{O}_2$ , H, and O, we used rate expressions with reasonable prefactors and barriers that are consistent with the room temperature rate measurements of McFadden and coworkers (Tsai *et al.*, 1989; Tsai and McFadden, 1990) and Peeters *et al.* (1992). We note that to date we have (mis)assigned the products of the reaction  $\bullet\text{CF} + \text{H} \rightarrow \text{C} + \text{HF}$  (about 25 kJ/mol exothermic) as  $\text{CH} + \text{F}$  (about 20 kJ/mol endothermic). This was done to eliminate C,  $\text{C}_2\text{H}$ ,  $\text{C}_4\text{H}_2$ , and other fuel rich species in order to minimize the number of species in the reaction set. If a hydrocarbon sub-mechanism is used that includes these species, the correct product channel should be used. For  $\bullet\text{CF} + \text{OH} \rightarrow \text{CO} + \text{HF}$ , we assumed that there was no barrier to reaction. For  $\bullet\text{CF} + \text{H}_2\text{O} \rightarrow \text{Products}$ , we estimated an activation energy of 70 kJ/mol by analogy to other Radical +  $\text{H}_2\text{O}$  reactions.  $\bullet\text{CF}$  can also be formed via  $\text{CH} + \text{HF} \rightarrow \bullet\text{CF} + \text{H}_2$  (roughly 70 kJ/mol exothermic). For reaction of  $\bullet\text{CF}$  with other molecules, we assumed upper limits that should be re-examined if those reactions are observed to contribute to  $\bullet\text{CF}$  destruction.

In the reaction set, fluoromethylidyne ( $\bullet\text{CF}$ ) is largely destroyed via reaction with  $\text{O}_2$  and OH. Reaction with H atoms and  $\text{H}_2\text{O}$  are minor channels. Given that there is no experimental measurements for reaction of  $\bullet\text{CF}$  with  $\text{H}_2\text{O}$ , limited (and inconsistent) data for reaction with  $\text{O}_2$ , and both of these reactions are likely to have modest barriers, these reactions provide a significant uncertainty to this reaction set. Further refinements of this mechanism should address these issues for :CHF, :CF<sub>2</sub>, and  $\bullet\text{CF}$ .

### 3.3.10. Carbonyl Fluoride Chemistry

An important set of species to fluorocarbon species are the carbonyl fluorides ( $\text{CHF}=\text{O}$ ,  $\text{CF}_2\text{O}$ ,  $\cdot\text{CF}=\text{O}$ ).  $\text{CHF}=\text{O}$  can be destroyed via unimolecular decomposition and H atom abstraction by H, O, and OH radicals. For the unimolecular decomposition (eliminating HF), we have fit the experimental data of Saito *et al.* (1985) using an extended Arrhenius expression (using the value for  $E_0$  (threshold energy) that they recommend based on their analysis). For the abstractions, we have substituted accepted rate expressions for the analogous  $\text{CH}_2=\text{O}$  reactions. However, there is some significant uncertainty for abstraction by H atoms. The C-H bond dissociation energy in  $\text{CHF}=\text{O}$  is about 45-50 kJ/mol stronger than in  $\text{CH}_2=\text{O}$ . Consequently, as an abstraction the barrier should be somewhat higher. On the other hand, H atom addition followed by H<sub>2</sub> elimination could be more facile than the pure abstraction.

$\text{CF}_2=\text{O}$  can be destroyed via unimolecular decomposition (F atom elimination), by reactions with H atoms, through reactions with OH radicals, and through reactions, potentially, with  $\text{H}_2\text{O}$ . The unimolecular decomposition is likely a minor channel due to the strong C-F bond. There are a number of possible reactions with H atoms: 1) direct abstraction of a F atom abstraction; 2) addition to the oxygen followed by 1,2 elimination of HF; and 3) addition to the carbon followed by 1,1 elimination of HF. Biordi *et al.* (1974) have estimated a rate constant for the net reaction of H with  $\text{CF}_2=\text{O}$  at 1800 K based on their molecular beam sampling measurements in low pressure flames. More recently, Richter *et al.* (1994) have estimated a rate expression based upon measurements at several different temperatures. We have also BAC-MP4 *ab initio* transition state calculations (Zachariah *et al.*, 1995) followed by RRKM analysis to provide rate expressions for each of the possible channels. Our calculations are in excellent agreement with the experimental values and indicate that the addition/1,2 elimination channel dominates (92 kJ/mol barrier), the addition/1,1 elimination channel is about a factor of ten slower (101 kJ/mol barrier), and the direct abstraction channel is negligible (188 kJ/mol barrier).  $\text{CF}_2=\text{O}$  may also be destroyed via addition of OH to the carbon atom followed by 1,2-elimination of HF. However, this is likely a minor channel for destruction, since from our BAC-MP4 *ab initio* transition state calculations (Zachariah *et al.*, 1995), we estimate a barrier of about 105 kJ/mol. Because of the low reactivity of  $\text{CF}_2=\text{O}$  and the large amounts of  $\text{H}_2\text{O}$

in hydrocarbon flames,  $\text{CF}_2\text{O} + \text{H}_2\text{O}$  reactions must be considered. We have calculated (Zachariah *et al.*, 1995) rate expressions for  $\text{CF}_2=\text{O} + \text{H}_2\text{O}$  complex formation followed by HF elimination. Modeling results suggest that it is a secondary destruction pathway to the H atom addition/1,2 elimination pathway, but, nevertheless, still needs to be considered.

• $\text{CF}=\text{O}$  can be destroyed via unimolecular decomposition and reactions with H, O, OH, and • $\text{CH}_3$  radicals. Modeling results suggest that the unimolecular decomposition and the reaction with H atoms are the primary decomposition pathways. For reaction with H atoms, we used a rate constant identical to that for the analogous HCO reaction. For the unimolecular decomposition, we determined a rate expression based on the reasonable assumption that combination reaction (reverse direction) is barrierless. There is significant uncertainty in the heat of formation of • $\text{CF}=\text{O}$  and, consequently, there is significant uncertainty in this rate. Future refinements of this mechanism should address this issue.

## 3.4. C<sub>2</sub> Fluorinated Hydrocarbon Chemistry

### 3.4.1. Overview

The C<sub>2</sub> subset of the reaction set (approximately 370 reactions) consists of chemistry of 34 species containing two carbons (and hydrogen/fluorine/oxygen) with H, O, OH, H<sub>2</sub>O, and other flame species (see reactions ED-xx, EC-xx, EA-xx, ER-xx, GG-xx, JD-xx, JA-xx, JO-xx, KK-xx, CF-xx in Table 5). The C<sub>2</sub>/H/F/O species used in this reaction set are the 9 fluoroethanes (*e.g.*, CH<sub>2</sub>F-CF<sub>3</sub>), the 11 fluoroethyl radicals (*e.g.*, CH<sub>2</sub>F-CF<sub>2</sub>•), the 6 fluoroethylenes (*e.g.*, CHF=CF<sub>2</sub>), the 7 fluorovinyl radicals (*e.g.*, CF<sub>2</sub>=CH•), the fluoroacetylenes (C<sub>2</sub>HF, C<sub>2</sub>F<sub>2</sub>), and the fluoroketenes and fluoroketyl radical (CHF=CO, CF<sub>2</sub>=CO, •CF=CO). This reaction set will not be described here in detail. Briefly, the fluoroethane destruction pathways (like fluoromethanes) consist of thermally and chemically activated decompositions and H atom abstraction reactions. Fluoroethyl radicals can react with H atoms creating fluoroethylenes via chemically activated fluoroethanes and HF elimination. Fluoroethyl radicals can also react with oxygen-containing species (O<sub>2</sub>, O, OH), resulting in the formation of oxidized fragments (*e.g.*, CF<sub>3</sub>-CF<sub>2</sub>• + O → •CF<sub>3</sub> + CF<sub>2</sub>=O). Fluoroethylenes (produced from thermally and chemically activated fluoroethane decompositions) are predominantly destroyed via reaction with O radicals, resulting in the formation of oxidized fragments (*e.g.*, CH<sub>2</sub>=CF<sub>2</sub> + O → •CH=O + •CHF<sub>2</sub>). Fluoroethylenes are also destroyed to a lesser degree through H atom abstraction by radicals such as OH, resulting in formation of fluorovinyl radicals (*e.g.*, CH<sub>2</sub>=CF<sub>2</sub> + OH → CF<sub>2</sub>=CH• + H<sub>2</sub>O). Fluorovinyl radicals (like fluoromethyl and fluoroethyl radicals) are destroyed via reactions with H radicals, as well as with oxygen-containing species.

### 3.4.2. Fluoroethanes: Thermally and Chemically Activated Decompositions

Both thermally and chemically activated decompositions of the fluoroethanes were considered, as well as stabilization of hot fluoroethanes (*e.g.*,  $\text{CH}_3\text{-CF}_3 \rightarrow \text{CH}_2=\text{CF}_2 + \text{HF}$ ,  $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_2=\text{CF}_2 + \text{HF}$ , and  $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_3\text{-CF}_3$ ). There have been quite a few measurements (mainly in shock tubes) of the unimolecular decomposition of the fluoroethanes. The kinetics of decomposition of most of the fluoroethanes (HF elimination) has been measured in a comprehensive series of work by Tschuikow-Roux and coworkers (Tschuikow-Roux *et al.*, 1970; Tschuikow-Roux and Quiring, 1971; Tschuikow-Roux *et al.*, 1971; Millward *et al.*, 1971; Millward and Tschuikow-Roux, 1972; Sekhar and Tschuikow-Roux, 1974). Data for HF elimination from the other fluoroethanes have been obtained by Kerr and Timlin (1971) and Trotman-Dickenson and coworkers (Day and Trotman-Dickenson, 1969; Cadman *et al.*, 1970). Fluoroethane decomposition kinetics have also been measured by a few other workers (Kochubei *et al.*, 1980; Mitin *et al.*, 1988). We selected experimental values from these and other sources and used them without modification. The validity of employing these high pressure limit values should be re-examined for those fluoroethanes which have only a few fluorine substitutions, especially when using the reaction set at low pressures (and high temperatures).

There have been a number of measurements for reactions of a few of the chemically activated or "hot" fluoroethanes produced by combination of fluoromethyl radicals by Kim *et al.* (1973), by Trotman-Dickenson and coworkers (Kirk *et al.*, 1968; Phillips and Trotman-Dickenson, 1968; Cadman *et al.*, 1976), and by Pritchard and coworkers (Pritchard *et al.*, 1964; Bryant and Pritchard, 1967; Bryant *et al.*, 1967; Pritchard and Thommarson, 1967; Perona *et al.*, 1968; Pritchard and Bryant, 1968; Pritchard and Perona, 1970; Follmer and Pritchard, 1974). Some of this work includes measurements of branching ratios between product channels (*i.e.*, HF elimination versus stabilization). There are no measurements (to our knowledge) for decomposition of hot fluoroethanes following combination of fluoroethyl radicals and H atoms. We used rate expressions for all of the hot fluoroethanes for the various product channels based on our RRKM calculations in order to provide a consistent set. Further refinements of this

mechanism should include using the existing experimental data as reference values for the RRKM calculations.

### 3.4.3. Fluoroethanes: Fluoromethyl Disproportionations, Fluoromethylene Insertions

There has been a number of measurements of disproportionations between methyl and fluoromethyl radicals (Pritchard and Follmer, 1973; Nilsson and Pritchard, 1982; Pritchard *et al.*, 1984, 1985, 1987, 1990, 1991, 1992). These studies suggest a branching ratio for disproportionation versus combination (HF elimination or stabilization) of about 10-20% at 350-500 K. We employed these data in combination with estimated barriers from our BAC-MP4 *ab initio* calculations and determined rate expressions consistent with the available experimental data. The activation energies or barriers-to-disproportionation are about 3-9 kJ/mol for reactions involving  $\cdot\text{CHF}_2$  (*i.e.*, :CF<sub>2</sub> product) and 14-19 kJ/mol for reactions involving  $\cdot\text{CH}_2\text{F}$  (*i.e.*, :CHF product). :CHF and :CF<sub>2</sub> may also insert into C-H bonds in methane and fluoromethanes. We used rate expressions based on estimated barriers from our BAC-MP4 *ab initio* calculations of 63 and 130 kJ/mol for insertions of :CHF and :CF<sub>2</sub>, respectively. These are rather significant when compared to :CH<sub>2</sub>, which inserts into C-H bonds with little barrier. Our BAC-MP4 *ab initio* calculations suggest these barriers result from ionic repulsion between the electropositive H atom on the (fluoro)methane and the highly electropositive carbon atom on the fluoromethylene. For example, the H atom on CH<sub>4</sub> has a Mulliken charge of +0.17 and the C atom on :CF<sub>2</sub> has a Mulliken charge of +0.54. However, there is some experimental evidence to suggest that the barriers are significantly smaller (DiFelice and Ritter, 1994). This apparent conflict for these important species should be addressed in future mechanism refinements.

### 3.4.4. Fluoroethanes: Abstractions

There have been quite a few measurements of H atom abstractions from fluoroethanes by OH radicals. Cohen and coworkers (Cohen and Benson, 1980; Cohen and Westberg, 1987) have used transition-state theory calculations to analyze and predict rate coefficients for a series of halogen-substituted methanes and ethanes. Much of their analysis is based on the experimental data of Clyne and Holt (1979) and Jeong *et al.* (1984). Other experimental data included in their analysis was from the measurements by Howard and Evenson (1976), Handwerk and Zellner (1978), Nip *et al.* (1979), and Martin and Paraskevopoulos (1983). In our work to date, we have used values recommended by Cohen and Benson (1987). For the three asymmetric fluoroethanes ( $\text{CH}_3\text{-CH}_2\text{F}$ ,  $\text{CH}_3\text{-CHF}_2$ ,  $\text{CH}_2\text{F-CHF}_2$ ), where there are different functional H substitutions, we have estimated the branching ratios (based on relative bond strengths). Recently, there have been a number of precise measurements for these abstraction reactions for a number of the fluoroethanes by Huie and coworkers (Liu *et al.*, 1990; Zhang *et al.*, 1992), by Ravishankara and coworkers (Talukdar *et al.*, 1991; Gierczak *et al.*, 1991), and by Nielsen (1991). Based on some of the more recent measurements there are newer recommendations by Cohen and Westberg (1991) for some of these reactions. The biggest changes are for reactions involving  $\text{CH}_3\text{-CHF}_2$  and  $\text{CHF}_2\text{-CF}_3$ . However, the changes in the rate expressions are only significant at temperatures well below flame temperatures (because of  $T^b$  dependence). These recommendations are based on experimental measurements at relatively low temperatures (about 300 K-500 K) and these reactions are primary decomposition pathways for the fluoroethanes at significantly higher temperatures. Consequently, it would be valuable to have experimental measurements of these rates at near flame temperatures. We note that based on our limited evaluation, the trends in the rate expressions for this homologous series appear to be consistent with changes in the number of H atoms and the C-H bond strengths or heats of reaction.

Although there have been a number of measurements of H atom abstractions by OH radicals from many of the fluoroethanes, there have been no measurements (to our knowledge) for H atom abstractions by H and O atoms from any of the fluoroethanes. Consequently, we utilized an empirical correlation that we determined for other H abstraction reactions (Burgess

*et al.*, 1994). For abstraction by H atoms, we used activation energies that were a factor of 2.5 times that for the analogous abstraction by OH radicals. For abstraction by O atoms, a factor of 2.7 was employed.

The fluoroethanes are largely destroyed via unimolecular decomposition and abstraction by OH radicals. Good quality experimental data are available. Future refinements of this mechanism need only to re-evaluate this work.

### 3.4.5. Fluoroethyl Radical Destruction

Fluoroethyl radicals can be destroyed via reaction with the flame species O<sub>2</sub>, H, O, OH, and •CH<sub>3</sub>. For reaction with O<sub>2</sub>, O, and OH, we used the accepted rate expressions for the analogous ethyl radical reactions. Reactions of fluoroethyl radicals with H atoms form hot fluoroethanes and we used rate expressions from our RRKM calculations as mentioned previously. Fluoroethyl radicals may combine with •CH<sub>3</sub> to form hot fluoropropanes (which most likely will be stabilized except at the highest temperature). Fluoroethyl radicals may also disproportionate with •CH<sub>3</sub> to form CH<sub>4</sub> and fluoroethylenes. The first channel (combination) was simply ignored in order to exclude C<sub>3</sub> fluorinated species from the reaction set. The rate constants for the second channel (disproportionation) were set identical to that accepted for the reaction  $\bullet\text{C}_2\text{H}_5 + \bullet\text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4$ .

### 3.4.6. Fluoroethylene Chemistry

There are experimental measurements (Simmie and Tschuikow-Roux, 1970; Simmie *et al.*, 1970) for the rate of pyrolysis of at least two of the fluoroethylenes (eliminating HF). For the other fluoroethylenes, we used these rate expressions as reference points and adjusted the activation energy based on the reaction enthalpy. For thermal decomposition or pyrolysis of perfluoroethylene ( $\text{CF}_2=\text{CF}_2 \rightarrow : \text{CF}_2 + : \text{CF}_2$ ), we used rate expressions from our RRKM fits to the experimental data of Schug and Wagner (1978). These data are also consistent with experimental rate expression of Modica and LaGraff (1966). For the other thermally and chemically activated fluoroethylene decompositions (*e.g.*,  $: \text{CHF} + : \text{CHF} \rightarrow \text{CHF}=\text{CHF}$  or  $\text{C}_2\text{HF} + \text{HF}$ ), we used rate expressions from our RRKM calculations (based on the reverse reaction or combination). Fluoroethylenes are primarily destroyed via reaction with O atoms (*e.g.*,  $\text{CH}_2=\text{CF}_2 + \text{O} \rightarrow \cdot \text{CHF}_2 + \text{HCO}$ ). For these reactions, we used the recommendations of Cveticanovic (1987). There is some evidence (Gilbert *et al.*, 1976) to suggest that the assumed methyl+formyl products (*e.g.*,  $\cdot \text{CHF}_2 + \text{HCO}$ ) may not be the only product channel (*e.g.*,  $\text{CHF}=\text{CHF} + \text{O} \rightarrow \text{CHF}=\text{C}=\text{O} + \text{HF}$  or  $\text{CHF}=\text{CHF} + \text{O} \rightarrow \text{CHF}=\text{O} + : \text{CHF}$ ). Future refinements of this mechanism should resolve this issue.

Fluoroethylenes can also be destroyed via reaction with H atoms. This includes H atom addition followed by stabilization of the fluoroethyl radical produced (*e.g.*,  $\text{CH}_2=\text{CF}_2 + \text{H} \rightarrow \text{CH}_3-\text{CF}_2\cdot$  or  $\text{CHF}_2-\text{CH}_2\cdot$ ), as well as H atom addition followed by F atom elimination (*e.g.*,  $\text{CH}_2=\text{CF}_2 + \text{H} \rightarrow \text{CH}_2=\text{CHF} + \text{F}$ ). There are some experimental data for these reactions, however, there appears to be some conflict between them. Consequently, in this mechanism, we simply employed an accepted rate expression for the H atom addition/stabilization for the analogous ethylene reaction. That is, we used rate expressions for the reactions of fluoroethylenes with H atoms by analogy to the recommendations of Tsang and Hampson (1986) for the two pathways  $\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_5$  and  $\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_3 + \text{H}_2$ .

For the F atom eliminations, we assumed barrierless addition in the reverse direction. However, there are some significant uncertainties here. First, it is likely the barrier to addition will be influenced by the degree of fluorine substitution on the alpha carbon. Secondly, the efficiency of stabilization of the chemically activated or "hot" fluoroethyl radical will be strongly

influenced by the degree of fluorine substitution. Fluoroethylenes may also be destroyed by OH addition/elimination reactions. This would result in the formation of (fluoro)vinoxy radicals (*e.g.*, CHO-CHF $\bullet$ ). However, in order to minimize the number of species in the reaction set, we have not considered these reactions. Future refinements of this mechanism should investigate whether or not these types of reactions significantly contribute to the chemistry.

Fluoroethylenes may also be destroyed via reaction with OH radicals. We have only considered H atom abstraction (and not addition/elimination). For abstraction of H atoms from the fluoroethylenes by OH radicals, we have used our fit (with an estimated T<sup>2.0</sup> dependence) to the values recommended by Baulch *et al.* (1992) for C<sub>2</sub>H<sub>4</sub> + OH → C<sub>2</sub>H<sub>3</sub> + H<sub>2</sub>O, which is based on a measurement by Tully (1988). Clearly the C-H bond strength will be significantly influenced by fluorine substitution. This issue should be addressed in future refinements of this mechanisms.

We have not considered another possible reaction pathway with OH; that is, OH addition followed by HF elimination (*e.g.*, CF<sub>2</sub>=CF<sub>2</sub> + OH → [•CF<sub>2</sub>-CF<sub>2</sub>-OH] → •CF<sub>2</sub>-CF=O). There are a number of uncertainties here and, consequently, this reaction pathway was simply not pursued (because of potential complexities). First, this pathway results in the production of a number of new species in the reaction set (fluorovinoxy radicals, *e.g.*, •CF<sub>2</sub>-CF=O), whose thermochemistry is unknown. Second, the effect of fluorine substitution on the barrier to OH addition is not known (but probably could be estimated reasonably well). Third, the relative rates for three competing reactions must be known; that is, 1) stabilization of the fluorohydroxyethyl radicals (*e.g.*, •CF<sub>2</sub>-CF<sub>2</sub>-OH), 2) reversion to reactants, and 3) HF elimination. Furthermore, if the fluorohydroxyethyl radicals are sufficiently stabilized, then they are a new set of species that must be considered. Fourth, there are a number of reactions which must be considered for the fluorovinoxy radicals. Future refinements of this mechanism should investigate the potential importance of the OH addition/HF elimination reactions for the fluoroethylenes. Most likely, only the perfluorocompounds may need to be considered (by analogy to the sole importance of the perfluoromethoxy radical).

There have been quite a few measurements of the reactions of O atoms with fluoroethylenes. These will not be reviewed here. In our work, we have used our fits to

extended Arrhenius form to the recommendations of Cvetanovic (1987) in order to extrapolate the low temperature values (300-500 K) to flame temperatures. A temperature dependence of  $T^{1.0}$  was used in analogy to other reactions. The recommended values by Cvetanovic are largely based on work in this area by Herron and Huie (1973), Jones and Moss (1974), Atkinson and Pitts (1977), and Gutman and coworkers (Park *et al.*, 1984).

For this class of reactions, it is generally understood that the dominant pathway is where the products are the fluoromethyl and (fluoro)formyl radical (*e.g.*  $\text{CH}_2=\text{CHF} + \text{O} \rightarrow \text{HCO} + \cdot\text{CH}_2\text{F}$ ) following dissociation of the chemically activated fluoroethylene oxide formed by O atom attack on the double bond. That is, the O atom first "adds" to the carbon with the least number of electronegative substituents (in this case F). An H atom on this carbon, then "migrates" to the other carbon. The numerous other possible channels are generally considered to be minor pathways: fluorine-substitute analogs of 1) stabilized ethylene oxide, 2) stabilized acetaldehyde, 3) formaldehyde + methylene, 4) acetyl radical + H, 5) ketene + H<sub>2</sub>, and 6) vinyl radical + OH. The latter, abstraction of H atom, is a separate reaction from the first four (addition/elimination). For completeness in the reaction set, we have included the latter abstraction reaction and used rate expressions based on analogy to the value estimated by Fontijn and coworkers (Mahmud *et al.*, 1987) for the unsubstituted ethylene reaction. It should be noted that for perfluoroethylene, the only possible channel is  $\text{CF}_2=\text{CF}_2 + \text{O} \rightarrow \text{CF}_2=\text{O} + :\text{CF}_2$  (*i.e.*, no H migration possible). It should also be noted that for  $\text{CH}_2=\text{CHF}$  there are two possible channels ("addition" of the O atom to one side or the other). We have used an estimated additional 4 kJ/mol for "addition" of the O atom to the fluorinated carbon. This is consistent with an upper limit measurement at room temperature for this reaction by Gutman and coworkers (Slagle *et al.*, 1974). Given that this is a primary decomposition pathway for the fluoroethylenes and that the rate expression that we have chosen to use is based on experimental measurements at low temperatures (300 K-500 K), it would be very valuable to have measurements of these reactions and product channels at near flame temperatures.

### **3.4.7. Fluorovinyl Radical Destruction**

Westmoreland (1992) has calculated the temperature (and pressure) dependencies of the rate for the chemically activated reaction  $\text{C}_2\text{H}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HCO}$ . We have used these values for the analogous fluorovinyl radical reactions. In our work, we have used the values recommended by Warnatz (1984) and Tsang and Hampson (1986) for the  $\text{C}_2\text{H}_3 + \text{O} \rightarrow \text{Products}$  and  $\text{C}_2\text{H}_3 + \text{OH} \rightarrow \text{Products}$  reactions, respectively, for the analogous fluorovinyl radical reactions. The values recommended by Warnatz for the first reaction is based on measurements by Heinemann *et al.* (1988).

### 3.4.8. Fluoroethyne, Fluoroketene, and Fluoroketyl Radical Chemistry

For reactions involving the fluoroethynes ( $C_2HF$ ,  $C_2F_2$ ), the fluoroketenes ( $CHF=C=O$ ,  $CF_2=C=O$ ), and the fluoroketyl radical ( $\cdot CF=C=O$ ), we have used rate expressions by analogy to the corresponding hydrocarbons ( $C_2H_2$ ,  $CH_2CO$ ,  $\cdot HCCO$ ). For reaction of H atoms with the two fluoroacetylenes ( $C_2HF$ ,  $C_2F_2$ ), we have used rate expressions derived from the recommendation of Warnatz (1984) for  $C_2H_2 + H \rightarrow C_2H_3$ , which is based on measurements by Payne and Stief (1976). For these H atom addition reactions, we employed third-body stabilization efficiencies and low pressure limits identical to that for acetylene. Future refinements of this mechanism should provide better estimates for these reactions.

### 3.5. BAC-MP4 *Ab Initio* Predictions

For a number of reactions considered in the mechanism, there are no or little experimental rate data. Consequently, we have estimated that data using BAC-MP4 *ab initio* calculations of the transition state geometries and energies and RRKM/master equation analysis. A short description of the BAC-MP4 *ab initio* calculations is given in the section titled Thermochemistry: BAC-MP4 *Ab Initio* Predictions. The transition state for a reaction was obtained by searching for a geometry with one negative eigenvalue. This corresponds to a saddle point on the potential energy surface. This is then followed by a steepest-descent reaction path analysis to ensure that the calculated transition state corresponds to the appropriate reactants and products. BAC corrections are then assigned in the same manner as with the equilibrium structures. In order to quantify the uncertainties in the calculated data, we have also performed calculations on a number of related reactions where there is good quality experimental data.

We have calculated transition states for a number of sets of reactions, including the following:

1. HF elimination from the fluoromethanes (*e.g.*, CH<sub>3</sub>F → :CH<sub>2</sub> + HF);
2. H<sub>2</sub> elimination from the fluoromethanes (*e.g.*, CH<sub>3</sub>F → :CHF + H<sub>2</sub>);
3. H atom abstraction by H from the fluoromethanes (*e.g.*, CH<sub>3</sub>F + H → •CH<sub>2</sub>F + H<sub>2</sub>);
4. F atom abstraction by H from the fluoromethanes (*e.g.*, CH<sub>3</sub>F + H → •CH<sub>3</sub> + HF);
5. reactions of H<sub>2</sub>O with the fluoromethylenes (*e.g.*, :CHF + H<sub>2</sub>O → CH<sub>2</sub>FOH → CH<sub>2</sub>O + HF);
6. reactions of H<sub>2</sub>O with carbonyl difluoride (*e.g.*, CF<sub>2</sub>=O + H<sub>2</sub>O → FCO<sub>2</sub>H + HF);
7. F atom abstraction by H from carbonyl difluoride (*i.e.*, CF<sub>2</sub>=O + H → •CF=O + HF);
8. H atom addition to carbonyl difluoride (*e.g.*, CF<sub>2</sub>=O + H → •CF<sub>2</sub>OH → •CF=O + HF);
9. OH addition to carbonyl difluoride (*i.e.*, CF<sub>2</sub>=O + OH → •OCF<sub>2</sub>(OH) → FC(O)O• + HF).

The *ab initio* geometries and energies of the transition states were then used as inputs to RRKM/master equation analysis in order to calculate rate expressions. The calculated rate expressions agree well with those derived from experimental measurements (where they exist). Further discussion of the *ab initio* transition state calculations can be found elsewhere (Zachariah *et al.*, 1995).

There is one reaction that is very important to the chemistry of fluorinated hydrocarbon destruction and where the calculated rate expression can be compared with good quality experimental measurements. The rate of reaction of H atoms with  $\text{CF}_2=\text{O}$  has been estimated based on measurements in flames of the rate of disappearance of carbonyl difluoride. Biordi *et al.* (1974) estimated a rate constant at 1800 K for this reaction in  $\text{CF}_3\text{Br}$  inhibited methane/oxygen/argon premixed flames. More recently, Richter *et al.* (1994) have determined rate coefficients at 1175-1490 K for this reaction in  $\text{CF}_3\text{H}$  inhibited hydrogen/oxygen/argon premixed flames.

The reaction of H atoms with  $\text{CF}_2=\text{O}$  has three distinct pathways, one is a direct abstraction and the other two are addition/elimination reactions.

First, H atoms can abstract fluorine (*i.e.*,  $\text{CF}_2=\text{O} + \text{H} \rightarrow \cdot\text{CF}=\text{O} + \text{HF}$ ). Our BAC-MP4 transition state calculations suggest a barrier of about 150 kJ/mol for this reaction and barriers of about 130-170 kJ/mol for F atom abstraction from the fluoromethanes. These barriers are consistent with that measured by Kochubei and Moin (1971) for F atom abstraction by H from  $\text{CF}_4$ . They reported an activation energy of about 190 kJ/mol at 1200 K-1600 K. This would suggest a barrier of about 160 kJ/mol assuming a  $T^2$  dependence to the rate.

The second pathway consists of H atom addition to the carbon atom on the carbonyl difluoride followed by 1,1 elimination of HF from the chemically activated fluoromethoxy intermediate (*i.e.*,  $\text{CF}_2=\text{O} + \text{H} \rightarrow [\text{CHF}_2\text{O}\cdot]^* \rightarrow \cdot\text{CF}=\text{O} + \text{HF}$ ). The third pathway is also an addition/elimination reaction, but consists of H atom addition in this case to the oxygen atom on the carbonyl difluoride followed by 1,2 elimination of HF from the "hot" hydroxyfluoromethyl intermediate ( $\text{CF}_2=\text{O} + \text{H} \rightarrow [\cdot\text{CF}_2\text{OH}]^* \rightarrow \cdot\text{CF}=\text{O} + \text{HF}$ ).

Our *ab initio* transition state calculations suggest barriers of about 50 kJ/mol and 65 kJ/mol for addition to the carbon and oxygen sides of the carbonyl difluoride, respectively. It is slightly more energetically favorable for the H atom to add to the carbon side. However, the subsequent 1,1 HF elimination step in this case in order to form the  $\cdot\text{CF}=\text{O}$  product involves a transition state that is an additional 80 kJ/mol higher (a total of 130 kJ/mol). The overall energetics of this pathway is significantly less favorable than the 1,2 HF elimination step that follows H atom addition to the oxygen side. This involves a transition state that is only

additional 15 kJ/mol higher (a total of 80 kJ/mol). We have derived rate expressions based on RRKM/master equation calculations using the geometries and energies of the *ab initio* transition states. These calculated rate expressions (Zachariah *et al.*, 1995) agree extremely well with the experimental rate constants reported by Biordi *et al.* (1974) and Richter *et al.* (1994).

Further discussion of the *ab initio* transition state calculations can be found elsewhere (Zachariah *et al.*, 1995).



## 4. Future Mechanism Refinement

### 4.1. Overview

The purpose of this section is to highlight uncertainties in the reaction set that may impact its ability to predict adequately the chemistry of fluorinated hydrocarbon destruction and the behavior of fluorinated hydrocarbon-inhibited hydrocarbon flames. We will mention known significant uncertainties, both those that may influence and those that are unlikely to influence the overall chemistry. For example, the heats of formation of many of the species must be estimated using empirical methods, such as group additivity. However, much of the chemistry of the destruction of fluorinated hydrocarbon species in hydrocarbon flames is irreversible. That is, it is the rates of mainly highly exothermic steps that are important and not thermodynamic considerations (free energies) or endothermic steps. For example, although there is significant uncertainty in the heat of formation of :CHF, this should have little impact on the chemistry in hydrocarbon flames, since :CHF is overwhelmingly destroyed through reactions with radicals such as H and OH, and not through unimolecular decompositions. In general, the uncertainties in the reaction set will only be highlighted here.

The reaction set presented here should be considered a framework for development of a model that accurately describes the decomposition of fluorinated hydrocarbons and their impact on hydrocarbon flame inhibition chemistry. It should not be considered a finished product, since to date there has been very little comparison of its predictions with experimental measurements. Future refinement and validation of the mechanism will require input from measurements of flame speed, flame temperature, concentration profiles, and temperature profiles in fluorinated hydrocarbon-inhibited flames.

In the reaction set or mechanism presented here, there are a number of species with uncertain thermochemistry and a number of reactions with uncertain rate expressions. These can be divided (arbitrarily) into several classes. 1) In most cases, the uncertainties are derived from the lack of direct or even indirect experimental data for these species and reactions. 2) In some cases, certain classes of species and reactions were not included in the reaction set, because of lack of experimental data and uncertainty in the chemistry. 3) In the other cases, experimental

data exist, but because of the magnitude of the reaction set, we have not yet verified that the rate expressions employed in the reaction set are fully consistent with the available experimental data.

For example, the JANAF recommended heat of formation for CHF=O is simply the average of the heats of formation of the analogous CH<sub>2</sub>=O and CF<sub>2</sub>=O. Consequently, there is significant uncertainty introduced from this procedure (bond dissociation energies are strongly dependent upon alpha-substitution), irrespective of the uncertainties in the heats of formation of the reference compounds. For example, using the heats of formation of CH<sub>4</sub> (-75 kJ/mol) and CH<sub>2</sub>F<sub>2</sub> (-453 kJ/mol), one would estimate using this procedure a heat of formation for CH<sub>3</sub>F of -264 kJ/mol that is 26 kJ/mol lower than the accepted value (-238 kJ/mol).

An analogous example for estimated rate constants is for the hydrogen abstraction CHF=O + H → •CF=O + H<sub>2</sub>. In this case, we have simply used an accepted rate expression for the analogous reaction CH<sub>2</sub>=O + H → HCO + H<sub>2</sub>. Given that the C-H bond dissociation energy in CHF=O is about 45-55 kJ/mol stronger than in CH<sub>2</sub>=O, it is likely that the barrier to abstraction for the CHF=O reaction is somewhat higher than the barrier for the CH<sub>2</sub>=O reaction. Although we have estimated that the barrier is about 10 kJ/mol higher (based upon trends in other halogen-substituted hydrocarbons), we have not (to date) employed this estimate because of some uncertainties. For example, it is likely that this reaction is not an abstraction, but rather an addition to the oxygen (*e.g.*, CH<sub>2</sub>=O + H → •CH<sub>2</sub>OH) followed by a 1,2-elimination of H<sub>2</sub>, because H atom abstractions by H should have a barrier closer to 40 kJ/mol (like CH<sub>4</sub> + H → •CH<sub>3</sub> + H<sub>2</sub>). Consequently, the effective "barrier" may not be significantly influenced by the C-H bond strength.

Another important example of uncertainties in rate constants can be found for H atom addition/stabilization to the fluoroethylenes (*e.g.*, CH<sub>2</sub>=CF<sub>2</sub> + H → CH<sub>3</sub>-CF<sub>2</sub>• and CHF<sub>2</sub>-CH<sub>2</sub>•). We have simply employed an accepted rate expression for the H atom addition/stabilization for the analogous C<sub>2</sub>H<sub>4</sub> + H → •C<sub>2</sub>H<sub>5</sub> reaction. However, there are some significant uncertainties here. First, it is likely the barrier to addition will be influenced by the degree of fluorine substitution on the alpha carbon. For example, the barrier to addition for the above reaction involving CH<sub>2</sub>=CF<sub>2</sub> may be on the order of 8 kJ/mol versus 30 kJ/mol for addition to the unsubstituted versus substituted carbon, respectively. Secondly, the efficiency with which the "hot" fluoroethyl radical is stabilized will be strongly influenced by the degree of fluorine

substitution (*e.g.*, CHF<sub>2</sub>-CF<sub>2</sub>• versus CH<sub>3</sub>-CHF•). The relative barriers to addition and relative stabilization efficiencies could be calculated satisfactorily using *ab initio* and RRKM methods, respectively. However, to date we have not done these calculations.



## 4.2. Thermochemistry

There are a number of other species in this reaction set that have significant uncertainties in their heats of formation, because of lack of direct experimental data.

The heat of formation of CH<sub>3</sub>F has been estimated based on trends in the heats of formation of the other fluoromethanes. Although CH<sub>3</sub>F is unlikely to be a key species in fluorinated hydrocarbon-inhibited hydrocarbon flames, as the simplest fluorinated hydrocarbon, its heat of formation is significant as a reference point for heats of formation of other fluorinated hydrocarbons. An experimentally derived heat of formation for CH<sub>3</sub>F would be very valuable.

The value recommended in the JANAF tables for the heat of formation of :CHF is based on the average of the heats of formation of :CH<sub>2</sub> and :CF<sub>2</sub>. Other values are based on estimates of bond dissociation energies or the absence of :CHF as a product in certain reactions (Staemmler, 1974; Hsu *et al.*, 1978; Pritchard *et al.*, 1984). Consequently, there are significant uncertainties introduced from these procedures (*i.e.*, bond dissociation energies are strongly dependent upon alpha-substitution). Most reactions that create or destroy :CHF are highly irreversible reactions (*e.g.*, :CHF + H → CH + HF) and, consequently, are unaffected by the energetics of the reactions. However, disproportionation reactions involving :CHF may proceed with small barriers and have modest heats of reaction (*e.g.*, •CH<sub>3</sub> + •CH<sub>2</sub>F → CH<sub>4</sub> + :CHF). For these reactions, the uncertainty in the heat of formation of :CHF may be important.

The literature value for the heat of formation of CF<sub>2</sub>=O is reported with a relatively low uncertainty. However, our BAC-MP4 *ab initio* calculations predict a value that is about 40 kJ/mol higher than the experimental number. Other *ab initio* calculations (Montgomery *et al.*, 1994; Schnieder and Wallington, 1994) using different approaches also predict a heat of formation for CF<sub>2</sub>=O that is higher (by about 30 kJ/mol) than the experimental value. There is reason to believe that there may have been side or wall reactions that complicated the measurement. Furthermore, the heats of formation of all the other oxygenated C<sub>1</sub> fluorocarbons (*e.g.*, CF<sub>3</sub>O•, •CF=O, etc.) are referenced to CF<sub>2</sub>=O. Because of these issues, both uncertainties in the experimental measurements and *ab initio* calculations warrant further examination. A new, reliable experimental measurement would be ideal.

The JANAF recommended heat of formation for  $\text{CHF=O}$  is based on the average of the heats of formation of the analogous  $\text{CH}_2=\text{O}$  and  $\text{CF}_2=\text{O}$ . Although this procedure introduces significant uncertainty, it may not be important, since there are relatively good experimentally derived rate expressions for thermal decomposition of formyl fluoride ( $\text{CHF=O} \rightarrow \text{CO} + \text{HF}$ ).

The literature value for the heat of formation of  $\text{CF}_2=\text{O}$  is reported with a relatively low uncertainty. However, our BAC-MP4 *ab initio* calculations predict a value that is about 40 kJ/mol higher than the experimental number. Other *ab initio* calculations (Montgomery *et al.*, 1994; Schnieder and Wallington, 1994) using different approaches also predict a heat of formation for  $\text{CF}_2=\text{O}$  that is higher (by about 30 kJ/mol) than the experimental value. There is reason to believe that there may have been side or wall reactions that complicated the measurement. Furthermore, the heats of formation of all the other oxygenated  $\text{C}_1$  fluorocarbons (e.g.,  $\text{CF}_3\text{O}\cdot$ ,  $\cdot\text{CF=O}$ , etc.) are referenced to  $\text{CF}_2=\text{O}$ . Because of these issues, both uncertainties in the experimental measurements and *ab initio* calculations warrant further examination. A new, reliable experimental measurement would be ideal.

The value recommended in the JANAF tables for the heat of formation of  $\cdot\text{CF=O}$  is based on estimates of the C-F bond dissociation energy in  $\text{CF}_2=\text{O}$ . In contrast to that for  $\text{CHF=O}$ , the heat of formation of  $\cdot\text{CF=O}$  is important, since there are no experimental data for the unimolecular decomposition  $\cdot\text{CF=O} \rightarrow \text{CO} + \text{F}$ , which is a primary destruction pathway for  $\cdot\text{CF=O}$  (competing with H atom combination followed by HF elimination). Therefore, it would be very useful to obtain a better value (smaller uncertainty) for the heat of formation of  $\cdot\text{CF=O}$  that is based on some type of experimental measurement.

There are no experimentally derived heats of formation for many of the fluoroethanes ( $\text{CH}_3\text{-CH}_2\text{F}$ ,  $\text{CHF}_2\text{-CHF}_2$ ,  $\text{CH}_2\text{F-CF}_3$ ). These have been estimated using bond additivity, group additivity, or other empirical trends in heats of formation. However, there are significant uncertainties in using these procedures, because of non-covalent or ionic contributions to the stability of these species due the high electronegativity of fluorine. Furthermore, the stability of the fluoroethanes will influence product channels for fluoromethyl combination reactions (e.g.,  $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_3\text{-CF}_3$  versus  $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_2=\text{CF}_2 + \text{HF}$ ).

There are experimentally derived heats of formation (*i.e.*, heat of reaction data) for only three of the fluoroethyl radicals ( $\text{CH}_3\text{-CF}_2\bullet$ ,  $\text{CF}_3\text{-CH}_2\bullet$ ,  $\text{CF}_3\text{-CF}_2\bullet$ ). Values for the eight other fluoroethyl radicals have been estimated using heats of formation of the parent fluoroethanes (which in some cases are also estimates) and C-H and C-F bond dissociation energies (largely estimates). The stability of the fluoroethyl radicals can be of importance for destruction of fluoroethylenes (*e.g.*,  $\text{CH}_2=\text{CF}_2 + \text{H} \leftrightarrow \text{CH}_3\text{-CF}_2\bullet$  and  $\text{CH}_3\text{-CF}_2\bullet + \text{H} \rightarrow \text{CH}_2=\text{CHF} + \text{HF}$ ).

There are no experimentally derived heats of formation for the fluorovinyl radicals and these values cannot be estimated empirically. Consequently, in this reaction set we have employed values that we have calculated using *ab initio* methods. However, the uncertainties in these values may not be significant, since these species are largely formed via H atom abstraction (by OH) and consumed via combination with flame radicals such as H atoms. One possible uncertainty here is the effect of reaction energy on product channels for combination of H atoms (*e.g.*  $\text{CF}_2=\text{CH}\bullet + \text{H} \rightarrow \text{CH}_2=\text{CF}_2$  [stabilized] versus  $\text{C}_2\text{HF} + \text{HF}$  [elimination]).

There are no experimentally derived heats of formation for the fluoroketenes ( $\text{CHF}=\text{C}=\text{O}$ ,  $\text{CF}_2=\text{C}=\text{O}$ ) and the fluoroketyl radical ( $\bullet\text{CF}=\text{C}=\text{O}$ ). In order to include these potential important species in the mechanism, it was necessary to use thermochemical data from our *ab initio* calculations. There are a number of reversible reactions involving these species that are important under stoichiometric to fuel rich conditions. Consequently, the uncertainties in the heats of formation of these species may contribute to uncertainties in flame speeds, flame temperatures, and flame products. These uncertainties should be better quantified in future mechanism refinements.



### **4.3. Kinetics**

A brief discussion of the major uncertainties in the rate expressions used in this mechanism can be found in each individual section.



## 5. Reaction Set

### 5.1. Description of Listing

The reaction set listing (Table 5) is divided into sets of similar reaction types (e.g., Fluoromethanes: thermally and chemically activated decompositions, Fluoromethanes: atom abstraction and metathesis, Fluoromethyls: oxidation, etc.). For each reaction, the reaction number and reaction are given and followed by the Arrhenius parameters. The listing is essentially a CHEMKIN II reaction input file (Kee *et al.*, 1989).

The reactions are numbered according to the following scheme.

HO-xx	Hydrogen/Oxygen Chemistry
HC-xx	Hydrocarbon Chemistry
HF-xx	Hydrogen/Oxygen/Fluorine Chemistry
MD-xx	Fluoromethanes: Thermal and Activated Decompositions
MA-xx	Fluoromethanes: Abstractions
NN-xx	Fluoromethyl, Fluoromethylene, Fluoromethylidne Chemistry
PP-xx	Carbonyl Fluorides and Fluoromethoxy Chemistry
ED-xx	Fluoroethanes: Thermal and Activated Decompositions
EC-xx	Hot Fluoroethanes & Fluoroethyls: Fluoromethylene Reactions
EA-xx	Fluoroethanes: Abstractions by X (H, O, OH)
ER-xx	Fluoroethanes: Abstractions by R (CxHy)
GG-xx	Fluoroethyl Chemistry
JD-xx	Fluoroethylenes: Thermal and Activated Decompositions
JA-xx	Fluoroethylenes: Additions and Abstractions
JO-xx	Fluoroethylenes & Fluorovinyls: Oxidations
KK-xx	Fluoroethynes & Fluoroketenes Chemistry
CF-xx	H Atom Abstractions by F

The symbol " = " in the reaction indicates a reversible reaction and the symbol " = >" indicates an irreversible reaction. For reference purposes, the heat of reaction is also given for a number of the reactions (but not all). In addition, a notation and references are given to provide traceability on each rate expression. A detailed legend for the notation given for each reaction is at the end of Table 5. For example in the listing,  $\text{CH}_3\text{F} + \text{H} = \text{CH}_2\text{F} + \text{H}_2$  (reaction MA-13) has Arrhenius parameters  $A=2.70\text{E}03$ ,  $b=3.00$ ,  $E/R=2667.$ , where the rate expression is  $k = A * T^b * \exp(-E/RT)$ . The units are  $A_1=\text{mol/s}$ ,  $A_2=\text{mol/cm}^3/\text{s}$ ,  $A_3=\text{mol/cm}^6/\text{s}$  (for first, second, and third order reactions, respectively),  $T=\text{K}$ ,  $E=\text{kJ/mol}$ , and  $R=8.314 \text{ J/mol/K}$  or  $1.987 \text{ cal/mol/K}$ . Please note  $1 \text{ cal} = 4.184 \text{ J}$  (for conversion from SI units). For this reaction example, the notation and references "xf", "75WES/DEH", and "nist" indicate that the rate expression is our fit to the experimental data of Westenberg and deHaas (1975).

A number of the unimolecular reactions have rate expressions with third-body efficiencies and/or low pressure fall-off parameters. For example,  $\text{H} + \text{O}_2 \rightarrow \text{HO}_2 + \text{M}$  (reaction HO-13) has explicit third-body efficiencies for  $\text{M} = \text{H}_2\text{O}, \text{CO}_2, \text{H}_2, \text{CO}$ , and  $\text{N}_2$ . An example, of a rate expression with low pressure fall-off parameters is the reaction  $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{M}$  (reaction HC-16), where "LOW" and "TROE" are low pressure and Troe fall-off parameters. The reader is referred to Kee *et al.* (1989) for more details on third-body efficiencies and fall-off parameters.

For reference purposes at the end of Table 5, the experimental rate expression ( $A=1.80E13, b=0.00, E/R=4803.$ ) and the temperature range ( $T=600-900\text{K}$ ) from this work (75WES/DEH) are also given. In some cases, where rate expressions were estimated relative to a reference reaction, the A-factor or activation energy were adjusted. For example in the listing, the reaction  $\text{CH}_3\text{F} + \text{C}_2\text{H}_3 = \text{CH}_2\text{F} + \text{C}_2\text{H}_4$  (reaction MA-20) has the notations "r CH3" and "E\*0.9". These indicate that an activation energy was used that was 90% of the activation energy for the analogous abstraction by  $\text{CH}_3$ , a reaction that is slightly more exothermic.

In order to reduce (slightly) the number of species in the reaction set, the isomers  $\text{CHF}=\text{CHF}(E)$ ,  $\text{CHF}=\text{CH}(E)$ , and  $\text{CHF}=\text{CF}(E)$  were excluded (retaining the Z isomers). The differences in energies and chemistries are sufficiently small that this is justified. We note that a number of the fluoroethanes and fluoroethyl radicals have both *trans* and *gauche* forms. In this work, we used thermochemistry for the most stable or *trans* isomers.

The hydrogen/oxygen and hydrocarbon reaction subsets of the mechanism are derived from the Miller-Bowman mechanism (Miller and Bowman, 1989) and consists of about 30 species and 140 reactions. Any other hydrocarbon mechanism could be used instead. For example, the GRIMECH set (Bowman *et al.*, 1995) is a recent hydrocarbon mechanism that accurately reproduces flame speeds for methane mixtures.

In this work, some modifications to the Miller-Bowman mechanism were made. All nitrogen-containing species and reactions were removed. A number of the rich species (*e.g.*,  $\text{C}_2\text{H}, \text{C}_4\text{H}_2$ ) were eliminated from the mechanism in order to keep the number of species in the mechanism to a manageable level. A number of species (*e.g.*,  $\text{CH}_3\text{OH}$ ) were also added to the mechanism. In addition to these addition and deletions, a number of rate constants for a number

of reactions (*e.g.*, CH<sub>3</sub>+OH) were adjusted to provide correct falloff and product-channel ratios. In this section of the reaction set, the notation for the reference is slightly different. For example, for CH<sub>4</sub> + H = CH<sub>3</sub> + H<sub>2</sub> (reaction HC-1), the notation "73CLA/DOV MBA004" means that this rate expression was determined by Clark and Dove (1973) and was reaction #4 in table A of the Miller-Bowman mechanism (Miller and Bowman, 1989). Where only the Miller-Bowman reference is given, either the expression is directly attributable to that work or the origins/traceability of the expression is not clear.



<i>H</i>	<i>O</i>	H2/O2 System: Combination, Decomposition			A	b	E/R	note	ref1	ref2	Hr
<i>1</i>	H	+ H	+ M	= H2	+ M	1.00E+18	-1.00	0.		MBA139	
		H2/0/	H2O/0/	CO2/0/							
<i>2</i>	H	+ H	+ H2	= H2	+ H2	9.20E+16	-0.60	0.		MBA140	
<i>3</i>	H	+ H	+ H2O	= H2	+ H2O	6.00E+19	-1.25	0.		MBA141	
<i>4</i>	H	+ H	+ CO2	= H2	+ CO2	5.49E+20	-2.00	0.		MBA142	
<i>5</i>	O	+ O	+ M	= O2	+ M	1.89E+13	0.00	-900.	86TSA/HAM	MBA145	
<i>6</i>	H	+ OH	+ M	= H2O	+ M	1.60E+22	-2.00	0.		MBA143	
		H2O/5/									
<i>7</i>	H	+ O	+ M	= OH	+ M	6.20E+16	-0.60	0.		MBA144	
		H2O/5/									
<b>H2/O2 System: Atom Transfers</b>											
<i>8</i>	O	+ OH	= O2	+ H	+ H	4.00E+14	-0.50	0.		81HOW/SMI	MBA132
<i>9</i>	O	+ H2	= OH	+ H	+ H2O	5.06E+04	2.67	3166.	88SUT/MIC	MBA133	
<i>10</i>	OH	+ OH	= O	+ OH	+ H2O	6.00E+08	1.30	0.		MBA138	
<i>11</i>	H2	+ O2	= OH	+ OH	+ OH	1.70E+13	0.00	24046.	71JAC/HOU	MBA130	
<i>12</i>	OH	+ H2	= H2O	+ H	+ H	1.17E+09	1.30	1825.	79COH/WES	MBA131	
<b>H2/O2 System: Peroxyl and Peroxide</b>											
<i>13</i>	H	+ O2 + M	= HO2	+ M		3.61E+17	-0.72	0.		MBA134	
		H2O/18.6/	CO2/4.2/	H2/2.9/	CO/2.1/	N2/1.3/					
<i>14</i>	H	+ HO2	= H2	+ O2		1.25E+13	0.00	0.		MBA146	
<i>15</i>	O	+ HO2	= O2	+ OH		1.40E+13	0.00	540.		MBA137	
<i>16</i>	OH	+ HO2	= H2O	+ O2		7.50E+12	0.00	0.		MBA135	
<i>17</i>	H2O2	+ M	= OH	+ OH + M		1.30E+17	0.00	22899.		MBA148	
<i>18</i>	H	+ HO2	= OH	+ OH		1.40E+14	0.00	540.		MBA136	
<i>19</i>	HO2	+ HO2	= H2O2	+ O2		2.00E+12	0.00	0.		MBA147	
<i>20</i>	H2O2	+ H	= HO2	+ H2		1.60E+12	0.00	1912.		MBA149	
<i>21</i>	H2O2	+ OH	= H2O	+ HO2		1.00E+13	0.00	906.		MBA150	

HC	C1 Hydrocarbons: Methane	A	b	E/R	note	refl	ref2	Hr
1	CH4 + H = CH3 + H2	2.20E+04	3.00	4404.		73CLA/DOV	MBA004	
2	CH4 + O = CH3 + OH	1.02E+09	1.50	4330.		86SUT/MIC	MBA005	
3	CH4 + OH = CH3 + H2O	1.60E+06	2.10	1238.		83BAU/CRA	MBA005	
4	CH4 + O2 = CH3 + HO2	7.90E+13	0.00	28183.		72SKU/LIF	MBA003	
5	CH4 + HO2 = CH3 + H2O2	1.80E+11	0.00	9411.		72SKU/LIF	MBA006	
C1 Hydrocarbons: Methyl								
6	CH3 + H (+M) = CH4 (+M)	6.00E+16	-1.00	0.		84WAR	MBA002	
	LOW/8.00E26 -3.0 0./					89STE/SMI		
SRI/0.45	977. 979./							
H2/2.0/	CO/2.0/ CO2/3.0/ H2O/5.0/							
7	CH3 + H = CH2 + H2	9.00E+13	0.00	7599.			MBA013	
8	CH3 + O = CH2O + H	8.00E+13	0.00	0.			MBA009	
9	CH3 + OH = CH2 + H2O	7.50E+06	2.00	2516.			MBA012	
10	CH3 + OH = CH3OH	2.24E+40	-8.20	5875.			87DEA/WES	
11	CH3 + OH = CH2OH + H	2.64E+19	-1.80	4060.			87DEA/WES	
12	CH3 + OH = CH3O + H	5.74E+12	-0.23	7011.			87DEA/WES	
13	CH3 + OH = CH2SING + H2O	8.90E+19	-1.80	4060.			87DEA/WES	
14	CH3 + O2 = CH3O + O	2.05E+18	-1.57	14710.			86TSA/HAM	MBA008
15	CH3 + HO2 = CH3O + OH	2.00E+13	0.00	0.			86TSA/HAM	MBA007
16	CH3 + CH3 (+M) = C2H6 (+M)	9.03E+16	-1.20	329.			88WAG/WAR	MBA001
	LOW/3.18E41 -7.0 2762./						88WAG/WAR	
TROE/0.6401	6927. 132./							
H2/2.0/	CO/2/ CO2/3.0/ H2O/5.0/							

Table 5. NIST HFC Mechanism

HC	C1 Hydrocarbons: Methylen (triplet)	A	b	E/R	note	ref1	ref2	Hr
17	CH2 + OH = CH2O	+ H	2.50E+13	0.00	0.		MBA026	
18	CH2 + O = CO	+ H+H	5.00E+13	0.00	0.		MBA043	
19	CH2 + CO2 = CH2O	+ CO	1.10E+11	0.00	503.		MBA042	
20	CH2 + O = CO	+ H2	3.00E+13	0.00	0.		MBA044	
21	CH2 + O2 = CO2	+ H+H	1.60E+12	0.00	503.		MBA045	
22	CH2 + O2 = CH2O	+ O	5.00E+13	0.00	4529.		MBA046	
23	CH2 + O2 = CO2	+ H2	6.90E+11	0.00	252.		MBA047	
24	CH2 + O2 = CO	+ H2O	1.90E+10	0.00	-503.		MBA048	
25	CH2 + O2 = CO	+ OH+H	8.60E+10	0.00	-252.		MBA049	
26	CH2 + O2 = HCO	+ OH	4.30E+10	0.00	-252.		MBA050	
27	CH2 + CH3 = C2H4	+ H	3.00E+13	0.00	0.		MBA072	
28	CH2 + CH2 = C2H2	+ H2	4.00E+13	0.00	0.		MBA114	
	C1 Hydrocarbons: Methylen (singlet)							
29	CH2SING + M = CH2	+ M	1.00E+13	0.00	0.		MBA106	
	H/0.0/							
30	CH2SING + H = CH2	+ H	2.00E+14	0.00	0.		MBA111	
31	CH2SING + O2 = CO	+ OH+H	3.00E+13	0.00	0.		MBA109	
32	CH2SING + H2 = CH3	+ H	7.00E+13	0.00	0.		MBA110	
33	CH2SING + CH4 = CH3	<del>10</del> CH3	4.00E+13	0.00	0.		MBA107	
34	CH2SING + C2H6 = CH3	+ C2H5	1.20E+14	0.00	0.		MBA108	
	C1 Hydrocarbons: Methylidyne							
35	CH2 + H = CH	+ H2	1.00E+18	-1.56	0.		MBA024	
36	CH2 + OH = CH	+ H2O	1.13E+07	2.00	1510.		MBA025	
37	CH + O2 = HCO	+ O	3.30E+13	0.00	0.		MBA027	
38	CH + O = CO	+ H	5.70E+13	0.00	0.		MBA028	
39	CH + OH = HCO	+ H	3.00E+13	0.00	0.		MBA029	
40	CH + CO2 = HCO	+ CO	3.40E+12	0.00	347.		MBA030	
41	CH + H2O = CH2O	+ H	1.17E+15	-0.75	0.		MBA032	
42	CH + CH2O = CH2CO	+ H	9.46E+13	0.00	-259.		MBA033	
43	CH + CH2 = C2H2	+ H	4.00E+13	0.00	0.		MBA035	
44	CH + CH3 = C2H3	+ H	3.00E+13	0.00	0.		MBA036	
45	CH + CH4 = C2H4	+ H	6.00E+13	0.00	0.		MBA037	
46	C2H3 + CH = CH2	+ C2H2	5.00E+13	0.00	0.		MBA086	
47	HCCO + CH = C2H2	+ CO	5.00E+13	0.00	0.		MBA104	

HC	Oxidized C1 Hydrocarbons: Methanol	A	b	E/R	note	ref1	ref2	Hr
48	CH3OH + H = CH3O + H2	8.00E+12	0.00	3067.		90NOR		
49	CH3OH + OH = CH3O + H2O	1.50E+13	0.00	2999.		75BOW		
50	CH3OH + CH3 = CH3O + CH4	1.45E+01	3.10	3490.		90NOR		
51	CH3OH + O2 = CH2OH + HO2	2.05E+13	0.00	22505.		90NOR		
52	CH3OH + H = CH2OH + H2	3.20E+13	0.00	3067.		90NOR		
53	CH3OH + O = CH2OH + OH	3.88E+05	2.50	1550.		90NOR		
54	CH3OH + OH = CH2OH + H2O	1.50E+13	0.00	2999.		75BOW		
55	CH3OH + HO2 = CH2OH + H2O2	3.98E+13	0.00	9763.		90NOR		
56	CH3OH + CH3 = CH2OH + CH4	3.19E+01	3.17	3609.		90NOR		
<b>Oxidized C1 Hydrocarbons: Methoxy, Hydroxymethyl</b>								
57	CH3O + M = CH2O + H + M	1.00E+14	0.00	12582.			MBA014	
58	CH3O + O2 = CH2O + HO2	6.30E+10	0.00	1309.			MBA022	
59	CH3O + H = CH2O + H2	2.00E+13	0.00	0.			MBA016	
60	CH3O + O = CH2O + OH	1.00E+13	0.00	0.			MBA020	
61	CH3O + OH = CH2O + H2O	1.00E+13	0.00	0.			MBA018	
62	CH2OH + M = CH2O + H+M	1.00E+14	0.00	12582.			MBA015	
63	CH2OH + O2 = CH2O + HO2	1.48E+13	0.00	755.			MBA023	
64	CH2OH + H = CH2O + H2	2.00E+13	0.00	0.			MBA017	
65	CH2OH + O = CH2O + OH	1.00E+13	0.00	0.			MBA021	
66	CH2OH + OH = CH2O + H2O	1.00E+13	0.00	0.			MBA019	
<b>Oxidized C1 Hydrocarbons: Formaldehyde and Formyl</b>								
67	CH2O + M = HCO + H + M	3.31E+16	0.00	40765.			80DEA/JOH	
68	CH2O + H = HCO + H2	2.19E+08	1.77	1510.			86TSA/HAM	
69	CH2O + O = HCO + OH	1.80E+13	0.00	1550.			80KLE/SKO	
70	CH2O + OH = HCO + H2O	3.43E+09	1.18	-225.			86TSA/HAM	
71	HCO + M = CO + H+M	2.50E+14	0.00	8456.			84WAR	
	CO/1.9 / H2/1.9/ CH4/2.8/ CO2/3.0/ H2O/5.0/							
72	HCO + H = CO + H2	1.19E+13	0.25	0.			MBA057	
73	HCO + O = CO + OH	3.00E+13	0.00	0.			MBA058	
74	HCO + O = CO2 + H	3.00E+13	0.00	0.			MBA059	
75	HCO + OH = CO + H2O	1.00E+14	0.00	0.			84TEM/WAG	
76	HCO + O2 = CO + HO2	3.30E+13	-0.40	0.			81VEY/LES	
<b>Oxidized C1 Hydrocarbons: Carbon Monoxide</b>								
77	CO + O + M = CO2 + M	6.17E+14	0.00	1510.			86TSA/HAM	
78	CO + OH = CO2 + H	1.51E+07	1.30	-381.			MBA062	
79	CO + O2 = CO2 + O	1.60E+13	0.00	20634.			MBA063	
80	CO + HO2 = CO2 + OH	5.80E+13	0.00	11542.			MBA064	

Table 5. NIST HFC Mechanism

Table 5. NIST HFC Mechanism

<i>HC</i>	<i>C2</i> Hydrocarbons: Ethane		<b>A</b>	<b>b</b>	E/R	note	ref1	ref2	Hr
81	C2H6 + H = C2H5 + H2		5.40E+02	3.50	2622.		73CAL/DOW	MBA066	
82	C2H6 + O = C2H5 + OH		3.00E+07	2.00	2574.		84VAR	MBA067	
83	C2H6 + OH = C2H5 + H2O		8.70E+09	1.05	911.		83TUL/RAV	MBA068	
84	C2H6 + CH3 = C2H5 + CH4		5.50E-01	4.00	4177.		73CLA/DOW	MBA065	
<b>C2</b> Hydrocarbons: Ethyl									
85	C2H5 + H = CH3 + CH3		1.00E+14	0.00	0.				
86	C2H5 + O = CH2O + CH3		1.60E+13	0.00	0.				
87	C2H5 + O2 = C2H4+HO2		2.56E+19	-2.77	995.				
<b>C2</b> Hydrocarbons: Ethylene									
88	C2H4 + M = C2H2 + H2 + M		1.50E+15	0.00	28083.		83KIE/KAP	MBA128	
89	C2H4 + M = C2H3 + H + M		1.40E+16	0.00	41449.			MBA129	
90	C2H4 + H (+M) = C2HS (+M)		8.40E+08	1.50	498.		86TSA/HAM		
	LOW/6.37E27 -2.8 -54./								
	H2/2.0/ CO/2.0/ CO2/3.0/ H2O/5.0/								
91	C2H4 + H = C2H3 + H2		1.10E+14	0.00	4278.		73PEE/MAH	MBA073	
92	C2H4 + O = CH3 + HCO		1.60E+09	1.20	375.		84VAR	MBA073	
93	C2H4 + OH = C2H3 + H2O		4.50E+06	2.00	1434.	rf			
<b>C2</b> Hydrocarbons: Vinyl									
94	C2H3 + H = C2H2 + H2		1.20E+13	0.00	0.		92BAU/COB	MBA083	
95	C2H3 + OH = C2H2 + H2O		5.00E+12	0.00	0.			MBA084	
96	C2H3 + CH2 = C2H2 + CH3		3.00E+13	0.00	0.				
97	C2H3 + O2 = CH2O + HCO		1.05E+38	-8.22	3538.	a/s	92WES		
98	C2H3 + O2 = CH2O + HCO		4.48E+26	-4.55	2758.	direct	92WES		
99	C2H3 + O = CH2CO + H		3.00E+13	0.00	0.		84VAR	MBA081	
<b>C2</b> Hydrocarbons: Acetylene									
100	C2H2 + H (+M) = C2H3 (+M)		5.54E+12	0.00	1213.		76PAY/STI	MBA079	
	LOW/2.67E27 -3.5 2410./								
	H2/2.0/ CO/2.0/ CO2/3.0/ H2O/5.0/								
101	C2H2 + OH = HCCOH + H		5.04E+05	2.30	6794.			MBA088	
102	C2H2 + OH = CH2CO + H		2.18E-04	4.50	-503.			MBA089	
103	C2H2 + OH = CH3 + CO		4.83E-04	4.00	-1007.			MBA090	
104	C2H2 + O = CH2 + CO		1.02E+07	2.00	956.			MBA076	
105	C2H2 + O = HCCO + H		1.02E+07	956.				MBA077	
106	C2H2 + O2 = HCCO + OH		2.00E+08	1.50	15148.			MBA126	

Table 5. NIST HFC Mechanism

<i>HC</i>	Oxidized C2 Hydrocarbons: Ketene, HCCOH		<b>A</b>	<b>b</b>	E/R	note	refI	refII	Hr
<i>I07</i> HCCOH	+ H = CH2CO	+ H	1.00E+13	0.00	0.			MBA091	
<i>I08</i> CH2CO	+ H = CH3	+ CO	1.13E+13	0.00	1725.			MBA094	
<i>I09</i> CH2CO	+ H = HCCO	+ H2	5.00E+13	0.00	4026.			MBA095	
<i>I10</i> CH2CO	+ O = CO2	+ CH2	1.75E+12	0.00	679.			MBA093	
<i>I11</i> CH2CO	+ O = HCCO	+ OH	1.00E+13	0.00	4026.			MBA096	
<i>I12</i> CH2CO	+ OH = HCCO	+ H2O	7.50E+12	0.00	1007.			MBA097	
<i>I13</i> CH2CO	(+M) = CH2 + CO	(+M)	3.00E+14	0.00	35722.			MBA098	
	LOW/3.60E15	0.0	59270./						
<i>I14</i>	Oxidized C2 Hydrocarbons: Ketyl								
<i>I15</i> HCCO	+ H = CH2SING	+ CO	1.00E+14	0.00	0.			MBA101	
<i>I16</i> HCCO	+ O = H	+ 2CO	1.00E+14	0.00	0.			MBA102	
<i>I17</i> HCCO	+ O2 = 2CO	+ OH	1.60E+12	0.00	430.			MBA103	
<i>I18</i> HCCO	+ HCCO = C2H2	+ 2CO	1.00E+13	0.00	0.			MBA105	
<i>I19</i> HCCO	+ CH2 = C2H3	+ CO	3.00E+13	0.00	0.			MBA115	

Table 5. NIST HFC Mechanism

<i>HF</i>	H/F/O Chemistry			<i>A</i>	<i>b</i>	E/R	note	ref1	ref2	Hr
<i>1</i>	HF + M	= H	+ F	3.12E+13	0.00	49985.	xh	81BAU/DUX		135
<i>2</i>	H2 + F	= H	+ HF	2.56E+12	0.50	327.	xf	89STE/BRU	nist	-32
<i>3</i>	OH + F	= O	+ HF	2.00E+13	0.00	0.	r	H+HNO3	nist	-34
<i>4</i>	HO2 + F	= O2	+ HF	2.89E+12	0.50	0.	xf	83WAL/WAG	nist	-86
<i>5</i>	H2O + F	= OH	+ HF	1.30E+09	1.50	0.	xf	83WAL/WAG	nist	-17
<i>6</i>	H2O2 + F	= HO2	+ HF	1.73E+12	0.50	0.	xf	83WAL/WAG	nist	-49

<i>MD</i>	Fluoromethanes: Thermal Decomposition	<i>A</i>	<i>b</i>	E/R	note	ref1	ref2	Hr
7	CH2SING + HF == CH3F	1.91E+23	-3.62	896.	xg	73SCH/WAG	nist	-89
8	CHF + H2 == CH3F	2.25E+17	-2.85	6543.	ak		nist	-83
9	CH2F + H == CH3F	3.03E+21	-3.38	1741.	ak		nist	-97
10	CHF + HF == CH2F2	3.64E+24	-4.26	2043.	ak		nist	-72
11	CF2 + H2 == CH2F2	1.70E+06	-0.71	20584.	ak		nist	-62
12	CHF2 + H == CH2F2	2.75E+06	-0.32	3870.	ak		nist	-99
13	CHF3 + M == CF2 + HF	2.39E+30	-4.00	34751.	xg	91HID/NAK	nist	61
14	CF3 + F == CF4	1.60E+39	-7.90	4504.	xk	86PLU/RYA	nist	-130
Fluoromethanes: Activated Decomposition								
15	CH2F + H == CH2SING + HF	8.19E+15	-0.63	254.	ak		nist	-9
16	CH2F + H == CHF + H2	5.21E+08	1.16	503.	ak		nist	-15
17	CH2SING + HF == CHF + H2	2.08E+07	1.27	4192.	ak		nist	-6
18	CH3 + F == CH2SING + HF	1.62E+16	-0.88	-494.	k		nist	-18
19	CH3 + F == CH2F + H	1.36E+12	-0.39	-133.	k		nist	-9
20	CHF2 + H == CHF + HF	1.49E+14	-0.11	51.	ak		nist	-27
21	CHF2 + H == CF2 + H2	5.50E+03	2.42	-211.	ak		nist	-37
22	CHF + HF == CF2 + H2	5.77E+06	1.35	9009.	ak		nist	-10
23	CH2F + F == CHF + HF	5.00E+13	0.00	0.	k		nist	-46
24	CF3 + H == CF2 + HF	5.50E+13	0.00	0.	xk	89TSA/MCF	nist	-46
25	CHF2 + F == CF2 + HF	3.00E+13	0.00	0.	k		nist	-69
MA Fluoromethanes: H Atom Abstraction by H, O, OH, HO2								
1	CH3F + H == CH2F + H2	2.70E+03	3.00	2667.	xf	75WES/DEH	nist	-6
2	CH2F2 + H == CHF2 + H2	1.65E+03	3.00	2818.	xf	72RJD/DAV	nist	-4
3	CHF3 + H == CF3 + H2	9.00E+03	3.00	4680.	xf	78ART/BEL	nist	5
4	CH3F + O == CH2F + OH	6.50E+07	1.50	3523.	xf	67PAR/AZA	nist	-4
5	CH2F2 + O == CHF2 + OH	2.25E+07	1.50	3070.	xf	68PAR/NAL	nist	-2
6	CHF3 + O == CF3 + OH	1.00E+08	1.50	4655.	xf	78JOU/LEB	nist	7
7	CH3F + OH == CH2F + H2O	2.60E+08	1.50	1480.	xt	82JEO/KAU	91COH/WES	-20
8	CH2F2 + OH == CHF2 + H2O	2.80E+07	1.70	1278.	xt	82JEO/KAU	91COH/WES	-19
9	CHF3 + OH == CF3 + H2O	5.77E+06	1.80	2160.	xt	82JEO/KAU	87COH/BEN	-10
10	CH2F + H2O2 == CH3F + HO2	1.20E+10	0.00	-302.	r CH3	E*1.0	nist	-11
11	CHF2 + H2O2 == CH2F2 + HO2	1.20E+10	0.00	-302.	r CH3	E*1.0	nist	-13
12	CF3 + H2O2 == CHF3 + HO2	1.20E+10	0.00	-302.	r CH3	E*1.0	nist	-21

Table 5. NIST HFC Mechanism

MA	Fluoromethanes: F Atom Abstraction by H			A	b	E/R	note	ref1	ref2	Hr
I3 CH3F	+ H	= CH3	+ HF	2.75E+14	0.00	15803.	a		nist	-28
I4 CH2F2	+ H	= CH2F	+ HF	5.50E+13	0.00	17162.	a		nist	-17
I5 CHF3	+ H	= CHF2	+ HF	8.00E+13	0.00	20282.	a		nist	-5
I6 CF4	+ H	= CF3	+ HF	1.10E+15	0.00	22446.	x	71KOC/MOI	nist	-5
<b>Fluoromethanes: H Atom Abstraction by CH3, C2H3</b>										
I7 CH3F	+ CH3	= CH2F	+ CH4	1.50E+11	0.00	5737.	x	65PRU/BRY		-6
I8 CH2F2	+ CH3	= CHF2	+ CH4	8.70E+10	0.00	5133.	x	65PRU/BRY		-5
I9 CF3	+ CH4	= CHF3	+ CH3	8.34E+11	0.00	5496.	x	78ART/BEL		-4
I20 CH3F	+ C2H3	= CH2F	+ C2H4	1.50E+11	0.00	5184.	r CH3	E*0.9	nist	-10
I21 CH2F2	+ C2H3	= CHF2	+ C2H4	9.00E+10	0.00	4630.	r CH3	E*0.9	nist	-9
I22 CF3	+ C2H4	= CHF3	+ C2H3	8.00E+11	0.00	6039.	r CH3	E*1.1	nist	0
<b>Fluoromethanes: H Atom Abstraction by Fluoromethyls</b>										
I23 CH3F	+ CF3	= CH2F	+ CHF3	1.35E+12	0.00	5637.	x	67GIL/QUI		-10
I24 CH2F2	+ CH2F	= CHF2	+ CH3F	9.00E+10	0.00	7046.	r CH3	E*1.4	nist	1
I25 CH2F2	+ CF3	= CHF2	+ CHF3	7.20E+11	0.00	5637.	x	67GIL/QUI		-8
<b>Fluoromethanes: H Atom Abstraction from CH2O, CH3OH, HCO by Fluoromethyls</b>										
I26 CH2O	+ CH2F	= HCO	+ CH3F	5.54E+03	2.81	4177.	r CH3	E*1.4	nist	-9
I27 CH2O	+ CHF2	= HCO	+ CH2F2	5.54E+03	2.81	3926.	r CH3	E*1.3	nist	-10
I28 CH2O	+ CF3	= HCO	+ CHF3	5.54E+03	2.81	2315.	r CH3	E*.79	nist	-19
I29 HCO	+ CH2F	= CO	+ CH3F	9.00E+13	0.00	0.	r CH3		nist	-83
I30 HCO	+ CHF2	= CO	+ CH2F2	9.00E+13	0.00	0.	r CH3		nist	-84
I31 HCO	+ CF3	= CO	+ CHF3	9.00E+13	0.00	0.	r CH3		nist	-93
I32 HCO	+ CH2F	= CH2CO	+ HF	2.70E+13	0.00	0.	rul		nist	-82
I33 HCO	+ CHF2	= CHFCO	+ HF	2.70E+13	0.00	0.	rul		nist	-51
I34 HCO	+ CF3	= CF2CO	+ HF	2.70E+13	0.00	0.	rul		nist	-31

Table 5. NIST HFC Mechanism

NN	Fluoromethyls: Oxidation		A	b	E/R	note	ref1	ref2	Hr
<i>1</i>	CH2F + O2 = CHF:O + O+H		2.26E+09	1.14	14343. r CF3	dH	nist		28
<i>2</i>	CHF2 + O2 = CF2:O + O+H		2.26E+09	1.14	8304. r CF3	dH	nist		21
<i>3</i>	CF3 + O2 = CF3O + O		2.26E+09	1.14	10820. k		nist		
<i>4</i>	CH2F + O = CHF:O + H		5.70E+13	0.00	0. r CH3	CF3	nist		-91
<i>5</i>	CHF2 + O = CF2:O + H		3.70E+13	0.00	0. r CH3	CF3	nist		-103
<i>6</i>	CF3 + O = CF2:O + F		1.87E+13	0.00	0. x	89TSA/BEL	nist		-81
<i>7</i>	CH2F + OH = CH2O + HF		2.50E+13	0.00	0. r CH3		nist		-95
<i>8</i>	CHF2 + OH = CHF:O + HF		2.50E+13	0.00	0. r CH3		nist		-105
<i>9</i>	CF3 + OH = CF2:O + HF		2.00E+13	0.00	0. r CH3		nist		-115
<i>10</i>	CH2F + HO2 = CH3F + O2		3.00E+12	0.00	0. r CH3		nist		-49
<i>11</i>	CHF2 + HO2 = CH2F2 + O2		3.00E+12	0.00	0. r CH3		nist		-50
<i>12</i>	CF3 + HO2 = CHF3 + O2		2.00E+12	0.00	0. r CH3		nist		-59
<i>13</i>	CH2F + HO2 = CHF:O + OH + H		1.50E+13	0.00	0. r CH3		nist		-24
<i>14</i>	CHF2 + HO2 = CF2:O + OH + H		1.50E+13	0.00	0. r CH3		nist		-37
<i>15</i>	CF3 + HO2 = CF3O + OH		1.00E+13	0.00	0. r CH3		nist		-32

NN	Fluoromethylenes: Oxidation		A	b	E/R	note	ref1	ref2	Hr
16	CHF + H <sub>2</sub> O = CH <sub>2</sub> O + HF		5.00E+12	0.00	3271. a		nist	nist	29
17	CF <sub>2</sub> + H <sub>2</sub> O = CHF:O + HF		5.00E+12	0.00	12582. a		nist	nist	52
18	CHF + O <sub>2</sub> = CHF:O + O		2.00E+13	0.00	8304. r CF2	E-10	nist		-60
19	CF <sub>2</sub> + O <sub>2</sub> = CF <sub>2</sub> :O + O		2.01E+13	0.00	13337. x	77KEA/MAT			-51
20	CHF + O = CO + HF		8.43E+13	0.00	0. x	90TSA/MCF			-181
21	CF <sub>2</sub> + O = CF:O + F		7.00E+13	0.00	503. xf	90TSA/MCF	nist		-38
22	CHF + OH = HCO + HF		2.00E+13	0.00	0. r CF2		nist		-95
23	CF <sub>2</sub> + OH = CF:O + HF		2.00E+13	0.00	1761. r CF2		nist		
24	CHF + OH = CHF:O + H		2.00E+13	0.00	0. r CF2		nist		-78
25	CF <sub>2</sub> + OH = CF <sub>2</sub> :O + H		2.00E+13	0.00	1761. xf	78BIO/LAZ	nist		-68
26	CHF + HO <sub>2</sub> = CHF:O + OH		2.00E+13	0.00	0. ul		nist		
27	CF <sub>2</sub> + HO <sub>2</sub> = CF <sub>2</sub> :O + OH		2.00E+13	0.00	0. ul		nist		
28	CHF + HO <sub>2</sub> = CH <sub>2</sub> F + O <sub>2</sub>		5.00E+12	0.00	0. ul		nist		
29	CF <sub>2</sub> + HO <sub>2</sub> = CHF <sub>2</sub> + O <sub>2</sub>		5.00E+12	0.00	0. ul		nist		
<b>Fluoromethylenes: Destruction</b>									
30	CHF + H = CH + HF		2.95E+14	0.00	0. x	90TSA/MCF			-5
31	CF <sub>2</sub> + H = CF + HF		2.00E+14	0.00	629. xf	89TSA/MCF	nist		-12
32	CH <sub>2</sub> O + CHF = HCO + CH <sub>2</sub> F		1.00E+13	0.00	7549. r CH4		nist		1
33	CH <sub>2</sub> O + CHF = CH <sub>2</sub> CO + HF		1.00E+13	0.00	7549. r CH4		nist		-81
34	CH <sub>2</sub> O + CF <sub>2</sub> = HCO + CHF <sub>2</sub>		1.00E+13	0.00	20634. r CH4		nist		23
35	CH <sub>2</sub> O + CF <sub>2</sub> = CHFCO + HF		1.00E+13	0.00	20634. r CH4		nist		-28
36	HCO + CHF = CO + CH <sub>2</sub> F		2.00E+13	0.00	7549. r CH4		nist		-74
37	HCO + CF <sub>2</sub> = CO + CHF <sub>2</sub>		2.00E+13	0.00	20634. r CH4		nist		-52

Table 5. NIST HFC Mechanism

NN	Fluoromethylidyne: Oxidation	A	b	E/R	note	ref1	ref2	Hr
38	CF + O <sub>2</sub> = CF:O + O	2.00E+13	0.00	906. xf	92PEE/VAN	nist	-43	
39	CF + H <sub>2</sub> O = CHF:O + H	2.00E+13	0.00	8556. r Cl	90TSA/MCF	nist	-42	
40	CF + O = CO + F	4.00E+13	0.00	503. xf		nist	-128	
41	CF + OH = CO + HF	3.00E+13	0.00	503. r O		nist	-162	
42	CF + HO <sub>2</sub> = CF:O + OH	1.00E+13	0.00	0. ul		nist	-95	
<b>Fluoromethylidyne: Destruction</b>								
43	CH + HF = CF + H <sub>2</sub>	3.00E+13	0.00	0. r CH		nist	-17	
44	CF + H = CH + F	4.00E+13	0.00	377. xf	89TSA/MCF	nist		
45	CF + CH <sub>3</sub> = CH <sub>2</sub> :CF + H	3.00E+13	0.00	0. ul	use these products (correct) if C is in mechanism	nist	-20	
46	CF + C <sub>2</sub> H <sub>3</sub> = C <sub>2</sub> HF + CH <sub>2</sub>	3.00E+13	0.00	0. ul		nist	-9	
47	CF + CH <sub>2</sub> = C <sub>2</sub> HF + H	3.00E+13	0.00	0. ul		nist	-73	
48	CF + CH <sub>2</sub> SING = C <sub>2</sub> HF + H	3.00E+13	0.00	0. ul		nist	-82	
49	CF + CH <sub>4</sub> = CH <sub>2</sub> :CHF + H	5.00E+12	0.00	5033. ul		nist	-24	
50	CF + C <sub>2</sub> H <sub>4</sub> = C <sub>2</sub> H <sub>2</sub> + CH <sub>2</sub> F	1.00E+13	0.00	0. ul		nist	-27	
51	CF + F = CF <sub>2</sub>	6.00E+13	0.00	0. ul		nist	-123	
<b>PP Fluoromethoxy: Destruction</b>								
1	CF <sub>3</sub> O + M = CF <sub>2</sub> :O + F	9.03E+26	-3.42	10921. k		nist	17	
2	CF <sub>3</sub> O + H = CF <sub>2</sub> :O + HF	1.00E+14	0.00	0. ul		nist		
3	CF <sub>3</sub> O + H <sub>2</sub> = CF <sub>2</sub> :O + HF + H	1.00E+13	0.00	2516. ul		nist		
4	CF <sub>3</sub> O + H <sub>2</sub> O = CF <sub>2</sub> :O + HF + OH	1.00E+13	0.00	2516. ul		nist		
5	CF <sub>3</sub> O + CH <sub>4</sub> = CF <sub>2</sub> :O + HF + CH <sub>3</sub>	8.00E+12	0.00	1158. r C2H <sub>6</sub>	92CHE/ZHU	nist		
6	CF <sub>3</sub> O + C <sub>2</sub> H <sub>6</sub> = CF <sub>2</sub> :O + HF + C <sub>2</sub> H <sub>5</sub>	1.20E+13	0.00	1158. xf		nist		
7	CF <sub>3</sub> O + C <sub>2</sub> H <sub>4</sub> = CF <sub>2</sub> :O + HF + C <sub>2</sub> H <sub>3</sub>	1.00E+13	0.00	2516. ul		nist		
8	CF <sub>3</sub> O + C <sub>2</sub> H <sub>2</sub> = CF <sub>2</sub> :O + CH <sub>2</sub> :CF	1.00E+13	0.00	2516. ul		nist		
9	CF <sub>3</sub> O + CH <sub>2</sub> O = CF <sub>2</sub> :O + HF + HCO	5.00E+12	0.00	2516. ul		nist		
10	CF <sub>3</sub> O + HCO = CF <sub>2</sub> :O + HF + CO	5.00E+12	0.00	2516. ul		nist		

Table 5. NIST HFC Mechanism

<i>PP</i>	Carbonyl Fluorides: CHF=O, CF2=O		<b>A</b>	<b>b</b>	E/R	note	ref1	ref2	Hr
<i>I1</i>	CF:O + F = CF2:O		1.00E+12	0.00	0.				-131
<i>I2</i>	CF2:O + M = CO + HF		2.48E+25	-3.00	21641. xg		85SAI/KUR	nist	-2
<i>I3</i>	CF2:O + H2O = CO2 + 2HF		7.40E-03	3.84	12632. ak		th/FC(O)OH	nist	-13
<i>I4</i>	CF2:O + H = CF:O + HF		5.50E+08	1.42	9512. ak		Oadd	nist	-3
<i>I5</i>	CF2:O + H = CF:O + HF		1.20E+10	0.83	11223. ak		Cadd	nist	-3
<i>I6</i>	CF2:O + H = CF:O + HF		2.40E+07	1.88	18067. ak		abstract	nist	-3
<i>I7</i>	CF2:O + OH = CO2 + HF + F		2.70E+03	2.38	10569. ak		Oadd th/FCCO2	nist	-3
<i>I8</i>	CHF:O + H = CF:O + H2		1.10E+08	1.77	1510. r CH2O	A/2		nist	-4
<i>I9</i>	CHF:O + O = CF:O + OH		9.00E+12	0.00	1550. r CH2O			nist	-2
<i>20</i>	CHF:O + OH = CF:O + H2O		1.72E+09	1.18	-225. r CH2O			nist	-18
<i>21</i>	CF:O + H2O2 = CHF:O + HO2		1.00E+11	0.00	1963. r	E*0.56		nist	-13
<i>22</i>	CHF:O + CH3 = CF:O + CH4		2.00E+12	0.00	4529. rul			nist	-4
<i>23</i>	CHF:O + CH2F = CF:O + CH3F		2.00E+12	0.00	4529. rul			nist	2
<i>24</i>	CHF:O + CHF2 = CF:O + CH2F2		2.00E+12	0.00	4529. r			nist	1
<i>25</i>	CHF:O + CF3 = CF:O + CHF3		2.00E+12	0.00	4529. r			nist	-8
<i>26</i>	CHF:O + C2H3 = CF:O + C2H4		2.00E+12	0.00	2516. r	E*0.9		nist	-8
<b>Carbonyl Fluorides: CF=O</b>									
<i>27</i>	CO + F + M = CF:O + F + O		1.03E+19	-1.40	-245. k				
<i>28</i>	CF:O + O2 = CO2 + HF		2.00E+13	0.00	12079. ul			nist	33
<i>29</i>	CF:O + H = CO + HF		1.20E+14	0.00	r HCO			nist	25
<i>30</i>	CF:O + O = CO2 + F		3.00E+13	0.00	0. r HCO			nist	-102
<i>31</i>	CF:O + OH = CO2 + HF		3.00E+13	0.00	0. r HCO			nist	-94
<i>32</i>	CF:O + HO2 = CO2 + F + OH		3.00E+13	0.00	0. r HCO			nist	-128
<i>33</i>	CF:O + CH3 = CH2CO + HF		2.70E+13	0.00	0. ul			nist	-85
<i>34</i>	CF:O + CH2F = CHFCO + HF		2.70E+13	0.00	0. ul			nist	-52
<i>35</i>	CF:O + CHF2 = CF2CO + HF		2.70E+13	0.00	0. ul			nist	-35

<i>ED</i>	Fluoroethanes: Thermal Decomposition	<i>A</i>	<i>b</i>	E/R	note	ref1	ref2	Hr
<i>1</i>	CH3-CH2F + HF	2.63E+13	0.00	30146.	x	70CAD/DAY		11
<i>2</i>	CH3-CHF2 + HF	7.94E+13	0.00	31152.	x	70TSC/QUI		22
<i>3</i>	CH3-CF3 + HF	1.00E+14	0.00	34575.	x	71TSC/QUI		
<i>4</i>	CH2F-CH2F + HF	2.50E+13	0.00	31656.	x	71KER/TIM		5
<i>5</i>	CH2F-CHF2 + HF	1.26E+14	0.00	34776.	x	74SEK/TSC		
<i>6</i>	CH2F-CHF2 + HF	1.00E+13	0.00	32914.	x	74SEK/TSC		
<i>7</i>	CH2F-CF3 + HF	2.63E+13	0.00	35581.	x	72ML/TSC		8
<i>8</i>	CHF2-CHF2 + HF	2.00E+13	0.00	34927.	x	71ML/HAR		37
<i>9</i>	CHF2-CF3 + HF	4.00E+13	0.00	36034.	x	71TSC/MIL		32
								41
Fluoroethanes: Activated Decomposition, Ethyl + H (HF elimination)								
<i>10</i>	CH2F-CH2 + H	C2H4 = C2H4	+ HF	1.44E+20	-2.12	871.	k	
<i>11</i>	CH3-CHF + H	C2H4 = C2H4	+ HF	2.27E+20	-2.21	981.	k	nist
<i>12</i>	CH2F-CHF + H	CH2-CHF = CHF	+ HF	2.06E+23	-3.23	1147.	k	nist
<i>13</i>	CHF2-CH2 + H	CH2-CHF = CHF	+ HF	5.24E+16	-0.93	443.	k	nist
<i>14</i>	CH3-CF2 + H	CH2-CHF = CHF	+ HF	2.09E+16	-0.85	427.	k	nist
<i>15</i>	CHF2-CHF + H	CHF:CHF-Z = CHF	+ HF	1.86E+20	-2.29	881.	k	nist
<i>16</i>	CHF2-CHF + H	CH2:CF2 = CHF	+ HF	9.95E+19	-2.34	896.	k	nist
<i>17</i>	CH2F-CF2 + H	CHF:CHF-Z = CHF	+ HF	6.32E+19	-2.21	820.	k	nist
<i>18</i>	CH2F-CF2 + H	CH2:CF2 = CHF	+ HF	3.36E+19	-2.26	835.	k	nist
<i>19</i>	CF3-CH2 + H	CH2:CF2 = CHF	+ HF	1.12E+21	-2.27	1127.	k	nist
<i>20</i>	CHF2-CF2 + H	CHF:CF2 = CHF	+ HF	1.8IE+22	-2.92	1545.	k	nist
<i>21</i>	CF3-CF2 + H	CF2:CF2 = CHF	+ HF	1.4IE+21	-2.40	1827.	k	nist
Fluoroethanes: Activated Decomposition, Ethyl + H (methyl formation)								
<i>22</i>	CH2F-CH2 + H	CH3 = CH3	+ CH2F	3.80E+11	0.64	319.	k	
<i>23</i>	CH3-CHF + H	CH3 = CH3	+ CH2F	3.47E+10	0.90	689.	k	nist
<i>24</i>	CH2F-CHF + H	CH2F = CH2F	+ CH2F	1.79E+14	-0.11	664.	k	nist
<i>25</i>	CHF2-CH2 + H	CH3 = CH3	+ CHF2	2.02E+06	2.16	227.	k	nist
<i>26</i>	CH3-CF2 + H	CH3 = CH3	+ CHF2	1.62E+05	2.50	689.	k	nist
<i>27</i>	CHF2-CHF + H	CH2F = CH2F	+ CHF2	6.36E+12	0.32	735.	k	nist
<i>28</i>	CH2F-CF2 + H	CH2F = CH2F	+ CHF2	3.64E+12	0.33	594.	k	nist
<i>29</i>	CF3-CH2 + H	CH3 = CH3	+ CF3	2.48E+11	0.82	1444.	k	nist
<i>30</i>	CHF2-CF2 + H	CHF2 = CHF2	+ CF3	3.25E+15	-0.52	1510.	k	nist
<i>31</i>	CF3-CF2 + H	CF3 = CF3	+ CF3	4.37E+16	-0.75	2194.	k	nist

ED	Fluoroethanes: Activated Decomposition, Ethyl + H (stabilization)			b	E/R	note	ref1	ref2	Hr
32	CH2F-CH2	+ H	= CH3-CH2F	1.19E+35	-8.51	4097.	k	nist	
33	CH3-CHF	+ H	= CH3-CH2F	9.57E+38	-9.24	3704.	k	nist	
34	CH2F-CHF	+ H	= CH2F-CH2F	1.56E+45	10.80	4061.	k	nist	
35	CHF2-CH2	+ H	= CH3-CHF2	2.96E+37	-9.05	3603.	k	nist	
36	CH3-CF2	+ H	= CH3-CHF2	3.11E+40	-9.59	3619.	k	nist	
37	CHF2-CHF	+ H	= CH2F-CHF2	1.20E+45	-10.60	3785.	k	nist	
38	CH2F-CF2	+ H	= CH2F-CHF2	2.74E+43	-10.50	3860.	k	nist	
39	CF3-CH2	+ H	= CH3-CF3	7.27E+42	-9.86	3704.	k	nist	
40	CHF2-CF2	+ H	= CHF2-CHF2	3.77E+46	-10.80	4519.	k	nist	
41	CF3-CF2	+ H	= CHF2-CF3	1.12E+47	-10.80	2063.	k	nist	
	Fluoroethanes: Activated Decomposition, Ethyl + H (H atom elimination)								
42	CH2F-CH2	+ H	= CH3-CHF + H	1.87E+01	3.10	69.	k	nist	
43	CHF2-CH2	+ H	= CHF2-CH2 + H	1.59E-03	4.35	79.	k	nist	
44	CH2F-CF2	+ H	= CHF2-CHF + H	6.40E-01	3.53	921.	k	nist	
	Fluoroethanes: Activated Decomposition, Methyl + Methyl (HF elimination)								
45	CH3 + CH2F	= C2H4 + HF	2.35E+19	-1.86	941.	k	nist		
46	CH2F + CH2F	= CH2:CHF + HF	7.56E+21	-2.79	1303.	k	nist		
47	CH3 + CHF2	= CH2:CHF + HF	1.90E+15	-0.59	319.	k	nist		
48	CH2F + CHF2	= CHF:CHF-Z + HF	3.88E+20	-2.35	1453.	k	nist		
49	CH2F + CHF2	= CH2:CF2 + HF	2.23E+20	-2.41	1465.	k	nist		
50	CH3 + CF3	= CH2:CF2 + HF	5.53E+19	-1.94	1228.	k	nist		
51	CHF2 + CHF2	= CHF:CF2 + HF	2.20E+19	-1.95	2063.	k	nist		
52	CHF2 + CF3	= CF2:CF2 + HF	7.00E+16	-1.17	2179.	k	nist		
	Fluoroethanes: Activated Decomposition, Methyl + Methyl (stabilization)								
53	CH3 + CH2F	= CH3-CH2F	1.57E+31	-6.27	2235.	k	nist		
54	CH2F + CH2F	= CH2F-CH2F	2.37E+24	-3.79	1152.	k	nist		
55	CH3 + CHF2	= CH3-CHF2	1.93E+35	-7.69	2899.	k	nist		
56	CH2F + CHF2	= CH2F-CHF2	9.61E+38	-8.36	3493.	k	nist		
57	CH3 + CF3	= CH3-CF3	1.78E+33	-6.64	2526.	k	nist		
58	CHF2 + CHF2	= CHF2-CHF2	2.26E+24	-3.50	1691.	k	nist		
59	CHF2 + CF3	= CHF2-CF3	2.61E+26	-4.16	2063.	k	nist		
60	CF3 + CF3	= CF3-CF3	1.63E+36	-7.26	3548.	xvk	nist		

<i>EC</i>	Fluoroethanes: Methyl + Methyl Disproportionation (carbene formation)			E/R	note	refl	ref2	Hr
<i>1</i> CH3	+ CH2F	= CH4	+ CHF	3.00E+13	0.00	1711. r CF2	nist	
<i>2</i> CH2F	+ CH2F	= CH3F	+ CHF	3.00E+13	0.00	2416. r CF2	nist	
<i>3</i> CHF2	+ CH2F	= CH2F2	+ CHF	3.00E+13	0.00	2214. r CF2	nist	
<i>4</i> CF3	+ CH2F	= CHF3	+ CHF	3.00E+13	0.00	2315. r CF2	nist	
<i>5</i> CH3	+ CHF2	= CH4	+ CF2	3.00E+13	0.00	403. xfa	67BRY/PRI	
<i>6</i> CH2F	+ CHF2	= CH3F	+ CF2	3.00E+13	0.00	1107. xf	74FOL/PRI	
<i>7</i> CHF2	+ CHF2	= CH2F2	+ CF2	3.00E+13	0.00	805. xf	84PRI/NIL	
<i>8</i> CF3	+ CHF2	= CHF3	+ CF2	3.00E+13	0.00	1007. xf	69PRI/FOL	
<b>Fluoroethanes: Carbene Insertion into Fluoromethanes</b>								
<i>9</i> CH3F	+ CH2SING	= C2H4	+ HF	3.00E+13	0.00	0. r	nist	-101
<i>10</i> CH2F2	+ CH2SING	= CH2:CHF	+ HF	2.00E+13	0.00	0. r	nist	-91
<i>11</i> CHF3	+ CH2SING	= CH2:CF2	+ HF	1.00E+13	0.00	0. r	nist	-77
<i>12</i> CF4	+ CH2SING	= CHF:CF2	+ HF	4.00E+13	0.00	15601. a	nist	-62
<i>13</i> CH4	+ CHF	= C2H4	+ HF	4.00E+13	0.00	7549. a	nist	-66
<i>14</i> CH3F	+ CHF	= CH2:CHF	+ HF	3.00E+13	0.00	7549. r CH4	nist	-74
<i>15</i> CH2F2	+ CHF	= CH2:CF2	+ HF	1.00E+13	0.00	7549. r CH4	nist	-70
<i>16</i> CH2F2	+ CHF	= CHF:CHF-Z	+ HF	1.00E+13	0.00	7549. r CH4	nist	-63
<i>17</i> CHF3	+ CHF	= CHF:CF2	+ HF	1.00E+13	0.00	7549. r CH4	nist	-47
<i>18</i> CF4	+ CHF	= CF2:CF2	+ HF	4.00E+13	0.00	15601. a	nist	-30
<i>19</i> CH4	+ CF2	= CH2:CHF	+ HF	4.00E+13	0.00	20634. a	nist	-36
<i>20</i> CH3F	+ CF2	= CH2:CF2	+ HF	1.50E+13	0.00	20634. r CH4	nist	-49
<i>21</i> CH3F	+ CF2	= CHF:CHF-Z	+ HF	1.50E+13	0.00	20634. r CH4	nist	-42
<i>22</i> CH2F2	+ CF2	= CHF:CF2	+ HF	2.00E+13	0.00	20634. r CH4	nist	-37
<i>23</i> CHF3	+ CF2	= CF2:CF2	+ HF	1.00E+13	0.00	20634. r CH4	nist	-11
<i>24</i> CF4	+ CF2	= CF3-CF3		4.00E+13	0.00	25667. r CH4+10	nist	-56

<i>EC</i>	Fluoroethyls: Carbene Insertion into Fluoromethyls			<i>A</i>	<i>b</i>	E/R	note	ref1	ref2	Hr
25	CH2F	+ CH2	= CH2:CHF	+ H	4.00E+13	0.00	0.	r CH3		-66
26	CH2F	+ CH2	= C2H4	+ F	4.00E+13	0.00	0.	r CH3	nist	-54
27	CHF2	+ CH2	= CH2:CF2	+ H	4.00E+13	0.00	0.	r CH3	nist	-63
28	CHF2	+ CH2	= CH2:CHF	+ F	4.00E+13	0.00	0.	r CH3	nist	-47
29	CF3	+ CH2	= CH2:CF2	+ F	4.00E+13	0.00	0.	r CH3	nist	-41
30	CH2F	+ CH2SING	= CH2:CHF	+ H	4.00E+12	0.00	0.	r CH3	nist	-75
31	CH2F	+ CH2SING	= C2H4	+ F	2.00E+12	0.00	0.	r CH3	nist	-63
32	CHF2	+ CH2SING	= CH2:CF2	+ H	2.00E+12	0.00	0.	r CH3	nist	-72
33	CHF2	+ CH2SING	= CH2:CHF	+ F	4.00E+12	0.00	0.	r CH3	nist	-55
34	CF3	+ CH2SING	= CH2:CF2	+ F	6.00E+12	0.00	0.	r CH3	nist	-50
35	CH3	+ CHF	= CH2:CHF	+ H	1.00E+12	0.00	1007.	ul	nist	-46
36	CH2F	+ CHF	= CHF:CHF-Z	+ H	1.00E+12	0.00	1007.	ul	nist	-46
37	CH2F	+ CHF	= CH2:CHF	+ F	1.00E+12	0.00	1007.	ul	nist	-37
38	CHF2	+ CHF	= CHF:CF2	+ H	1.00E+12	0.00	1007.	ul	nist	-42
39	CHF2	+ CHF	= CHF:CHF-Z	+ F	1.00E+12	0.00	1007.	ul	nist	-27
40	CF3	+ CHF	= CHF:CF2	+ F	1.00E+12	0.00	2516.	ul	nist	-20
41	CH3	+ CF2	= CH2:CF2	+ H	1.10E+11	0.00	2617.	r	nist	-21
42	CH2F	+ CF2	= CHF:CF2	+ H	1.10E+11	0.00	2617.	r	nist	-20
43	CH2F	+ CF2	= CH2:CF2	+ F	1.10E+11	0.00	2617.	r	nist	-12
44	CHF2	+ CF2	= CF2:CF2	+ H	1.10E+11	0.00	2617.	r	nist	-6
45	CHF2	+ CF2	= CHF:CF2	+ F	1.10E+11	0.00	2617.	r	nist	-1

<i>E/A</i>	Fluoroethanes: H Atom Abstraction by H, O, OH			A	b	E/R	note	ref1	ref2	Hr
1	CH3-CH2F	+ H	= CH2F-CH2 + H2	5.50E+08	1.60	4580.	r OH	10AE+8	nist	2
2	CH3-CH2F	+ O	= CH2F-CH2 + OH	2.90E+08	1.60	3070.	r OH	5AE+5	nist	3
3	CH3-CH2F	+ OH	= CH2F-CH2 + H2O	5.50E+07	1.60	550.	rxt	91COH/WES	nist	-13
4	CH3-CH2F	+ H	= CH3-CHF + H2	3.30E+08	1.60	4580.	r OH	10AE+8	nist	
5	CH3-CH2F	+ O	= CH3-CHF + OH	1.60E+08	1.60	3070.	r OH	5AE+5	nist	
6	CH3-CH2F	+ OH	= CH3-CHF + H2O	3.30E+07	1.60	550.	rxt	91COH/WES	nist	
7	CH3-CHF2	+ H	= CHF2-CH2 + H2	1.50E+08	1.60	4831.	r OH	10A E+8	nist	
8	CH3-CHF2	+ O	= CHF2-CH2 + OH	7.50E+08	1.60	3322.	r OH	A*5 E+5	nist	
9	CH3-CHF2	+ OH	= CHF2-CH2 + H2O	1.54E+07	1.60	570.	rxt	91COH/WES	nist	
10	CH3-CHF2	+ H	= CH3-CF2 + H2	4.40E+07	1.60	4680.	r OH	A*10 E+8	nist	
11	CH3-CHF2	+ O	= CH3-CF2 + OH	2.20E+07	1.60	3171.	r OH	A*5 E+5	nist	
12	CH3-CHF2	+ OH	= CH3-CF2 + H2O	4.40E+06	1.60	670.	rxt	91COH/WES	nist	
13	CH3-CF3	+ H	= CF3-CH2 + H2	4.00E+10	1.10	6392.	r OH	A*10E+8	nist	3
14	CH3-CF3	+ O	= CF3-CH2 + OH	2.00E+10	1.10	4882.	r OH	A*5E+5	nist	4
15	CH3-CF3	+ OH	= CF3-CH2 + H2O	4.08E+09	1.10	2350.	xt	79CLY/HOL	87COH/BEN	-12
16	CH2F-CH2F	+ H	= CH2F-CHF + H2	6.00E+08	1.70	4831.	r OH	A*10 E+8	nist	-11
17	CH2F-CH2F	+ O	= CH2F-CHF + OH	3.00E+08	1.70	3322.	r OH	A*5 E+5	nist	-10
18	CH2F-CH2F	+ OH	= CH2F-CHF + H2O	6.16E+07	1.70	4932.	r OH	83MAR/PAR	91COH/WES	-26
19	CH2F-CHF2	+ H	= CHF2-CHF + H2	2.00E+08	1.70	4831.	r OH	A*10 E+8	nist	
20	CH2F-CHF2	+ O	= CHF2-CHF + OH	1.00E+08	1.70	3422.	r OH	A*5 E+5	nist	
21	CH2F-CHF2	+ OH	= CHF2-CHF + H2O	2.05E+07	1.70	906.	rxt	87COH/BEN	nist	
22	CH2F-CHF2	+ H	= CH2F-CF2 + H2	1.00E+08	1.70	5536.	r OH	A*10 E+8	nist	
23	CH2F-CHF2	+ O	= CH2F-CF2 + OH	5.00E+07	1.70	4026.	r OH	A*5 E+5	nist	
24	CH2F-CHF2	+ OH	= CH2F-CF2 + H2O	1.06E+07	1.70	1510.	rxt	87COH/BEN	nist	
25	CH2F-CF3	+ H	= CF3-CHF + H2	2.00E+08	1.70	5284.	r OH	A*10 E+8	nist	-2
26	CH2F-CF3	+ O	= CF3-CHF + OH	1.00E+08	1.70	3775.	r OH	A*5 E+5	nist	-1
27	CH2F-CF3	+ OH	= CF3-CHF + H2O	2.10E+07	1.70	1270.	xt	79CLY/HOL	87COH/BEN	-17
28	CH2F-CHF2	+ H	= CHF2-CF2 + H2	1.60E+07	1.70	5335.	r OH	A*10 E+8	nist	
29	CH2F-CHF2	+ O	= CHF2-CF2 + OH	8.00E+07	1.70	3825.	r OH	A*5 E+5	nist	
30	CH2F-CHF2	+ OH	= CHF2-CF2 + H2O	1.60E+07	1.70	1330.	xt	79CLY/HOL	87COH/BEN	
31	CH2F-CF3	+ H	= CF3-CF2 + H2	1.40E+07	1.60	5133.	r OH	A*10 E+8	nist	0
32	CH2F-CF3	+ O	= CF3-CF2 + OH	7.00E+07	1.60	3624.	r OH	A*5 E+5	nist	1
33	CH2F-CF3	+ OH	= CF3-CF2 + H2O	1.40E+07	1.60	1130.	xt	79CLY/HOL	87COH/BEN	-15
34	CF3-CF3	+ H	= CF3-CF2 + HF	1.00E+15	0.00	15098.	r CF4		nist	

Fluoroethanes: F Atom Abstraction by H

Table 5. NIST HFC Mechanism

Table 5. NIST HFC Mechanism

EA	Fluoroethanes: Association with HO <sub>2</sub>			A	b	E/R	note	ref1	ref2	Hr
<b>35</b>	CH3-CHF + H2O2	=	CH3-CH2F + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>36</b>	CH3-CF2 + H2O2	=	CH3-CHF2 + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>37</b>	CH2F-CH2 + H2O2	=	CH3-CH2F + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>38</b>	CH2F-CHF + H2O2	=	CH2F-CH2F + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>39</b>	CH2F-CF2 + H2O2	=	CH2F-CHF2 + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>40</b>	CHF2-CH2 + H2O2	=	CH3-CHF2 + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>41</b>	CHF2-CHF + H2O2	=	CH2F-CHF2 + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>42</b>	CHF2-CF2 + H2O2	=	CHF2-CHF2 + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>43</b>	CF3-CH2 + H2O2	=	CH3-CF3 + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>44</b>	CF3-CHF + H2O2	=	CH2F-CF3 + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	
<b>45</b>	CF3-CF2 + H2O2	=	CHF2-CF3 + HO <sub>2</sub>	9.00E+09	0.00	503.	r C2H5		nist	

Table 5. NIST HFC Mechanism

ER	Fluoroethanes: H Atom Abstraction by CH <sub>3</sub> , C2H <sub>3</sub>	A	b	E/R	note	ref1	ref2	Hr
<i>I</i>	CH <sub>3</sub> -CH <sub>2</sub> F + CH <sub>3</sub> = CH <sub>2</sub> F-CH <sub>2</sub> + CH <sub>4</sub>	2.00E+11	0.00	6744.	r	nist	nist	1
<i>2</i>	CH <sub>3</sub> -CH <sub>2</sub> F + C2H <sub>3</sub> = CH <sub>2</sub> F-CH <sub>2</sub> + C2H <sub>4</sub>	2.00E+11	0.00	5033.	r CH3	E-3	nist	4
<i>3</i>	CH <sub>3</sub> -CH <sub>2</sub> F + CH <sub>3</sub> = CH <sub>3</sub> -CHF + CH <sub>4</sub>	1.50E+11	0.00	5033.	r	nist	nist	
<i>4</i>	CH <sub>3</sub> -CH <sub>2</sub> F + C2H <sub>3</sub> = CH <sub>3</sub> -CHF + C2H <sub>4</sub>	1.50E+11	0.00	3523.	r CH3	E-3	nist	
<i>5</i>	CH <sub>3</sub> -CHF <sub>2</sub> + CH <sub>3</sub> = CHF <sub>2</sub> -CH <sub>2</sub> + CH <sub>4</sub>	2.00E+11	0.00	6039.	r	nist	nist	
<i>6</i>	CH <sub>3</sub> -CHF <sub>2</sub> + C2H <sub>3</sub> = CHF <sub>2</sub> -CH <sub>2</sub> + C2H <sub>4</sub>	2.00E+11	0.00	4529.	r CH3	E-3	nist	
<i>7</i>	CH <sub>3</sub> -CHF <sub>2</sub> + CH <sub>3</sub> = CH <sub>3</sub> -CF <sub>2</sub> + CH <sub>4</sub>	8.00E+10	0.00	5033.	r	nist	nist	
<i>8</i>	CH <sub>3</sub> -CHF <sub>2</sub> + C2H <sub>3</sub> = CH <sub>3</sub> -CF <sub>2</sub> + C2H <sub>4</sub>	8.00E+10	0.00	3523.	r CH3	E-3	nist	
<i>9</i>	CH <sub>3</sub> -CF <sub>3</sub> + CH <sub>3</sub> = CF <sub>3</sub> -CH <sub>2</sub> + CH <sub>4</sub>	2.00E+11	0.00	6039.	r	nist	nist	
<i>10</i>	CH <sub>3</sub> -CF <sub>3</sub> + C2H <sub>3</sub> = CF <sub>3</sub> -CH <sub>2</sub> + C2H <sub>4</sub>	2.00E+11	0.00	4529.	r CH3	E-3	nist	
<i>11</i>	CH <sub>2</sub> F-CH <sub>2</sub> F + CH <sub>3</sub> = CH <sub>2</sub> F-CHF + CH <sub>4</sub>	3.00E+11	0.00	5234.	r	nist	nist	5
<i>12</i>	CH <sub>2</sub> F-CH <sub>2</sub> F + C2H <sub>3</sub> = CH <sub>2</sub> F-CHF + C2H <sub>4</sub>	3.00E+11	0.00	3523.	r CH3	E-3	nist	-12
<i>13</i>	CH <sub>2</sub> F-CHF <sub>2</sub> + CH <sub>3</sub> = CHF <sub>2</sub> -CHF + CH <sub>4</sub>	2.00E+11	0.00	5033.	r	nist	nist	
<i>14</i>	CH <sub>2</sub> F-CHF <sub>2</sub> + C2H <sub>3</sub> = CHF <sub>2</sub> -CHF + C2H <sub>4</sub>	2.00E+11	0.00	3523.	r CH3	E-3	nist	
<i>15</i>	CH <sub>2</sub> F-CHF <sub>2</sub> + CH <sub>3</sub> = CH <sub>2</sub> F-CF <sub>2</sub> + CH <sub>4</sub>	1.00E+11	0.00	4831.	r	nist	nist	
<i>16</i>	CH <sub>2</sub> F-CHF <sub>2</sub> + C2H <sub>3</sub> = CH <sub>2</sub> F-CF <sub>2</sub> + C2H <sub>4</sub>	1.00E+11	0.00	3523.	r CH3	E-3	nist	
<i>17</i>	CH <sub>2</sub> F-CF <sub>3</sub> + CH <sub>3</sub> = CF <sub>3</sub> -CHF + CH <sub>4</sub>	2.00E+11	0.00	5033.	r	nist	nist	
<i>18</i>	CH <sub>2</sub> F-CF <sub>3</sub> + C2H <sub>3</sub> = CF <sub>3</sub> -CHF + C2H <sub>4</sub>	2.00E+11	0.00	3523.	r CH3	E-3	nist	
<i>19</i>	CHF <sub>2</sub> -CHF <sub>2</sub> + CH <sub>3</sub> = CHF <sub>2</sub> -CF <sub>2</sub> + CH <sub>4</sub>	3.00E+11	0.00	5033.	r	nist	nist	
<i>20</i>	CHF <sub>2</sub> -CHF <sub>2</sub> + C2H <sub>3</sub> = CHF <sub>2</sub> -CF <sub>2</sub> + C2H <sub>4</sub>	3.00E+11	0.00	3523.	r CH3	E-3	nist	
<i>21</i>	CHF <sub>2</sub> -CF <sub>3</sub> + CH <sub>3</sub> = CF <sub>3</sub> -CF <sub>2</sub> + CH <sub>4</sub>	5.70E+10	0.00	4781.	x	64PRI/THO	-1	
<i>22</i>	CHF <sub>2</sub> -CF <sub>3</sub> + C2H <sub>3</sub> = CF <sub>3</sub> -CF <sub>2</sub> + C2H <sub>4</sub>	6.00E+10	0.00	3523.	r CH3	E-3	nist	2

<i>ER</i>	Fluoroethanes: H Atom Abstraction by Fluoromethyls	<b>A</b>	<b>b</b>	E/R	note	ref1	ref2	Hr
23	CH3-CH2F + CH2F = CH2F-CH2 + CH3F	2.00E+11	0.00	6543.	r CH3		nist	6
24	CH3-CH2F + CH2F = CH3-CHF + CH3F	1.50E+11	0.00	5033.	r CH3		nist	
25	CH3-CHF2 + CH2F = CHF2-CH2 + CH3F	2.00E+11	0.00	6039.	r CH3		nist	
26	CH3-CHF2 + CH2F = CH3-CF2 + CH3F	8.00E+10	0.00	5033.	r CH3		nist	
27	CH3-CF3 + CH2F = CF3-CH2 + CH3F	2.00E+11	0.00	6039.	r CH3		nist	7
28	CH2F-CH2F + CH2F = CH2F-CHF + CH3F	3.00E+11	0.00	5033.	r CH3		nist	-7
29	CH2F-CHF2 + CH2F = CHF2-CHF + CH3F	2.00E+11	0.00	5033.	r CH3		nist	
30	CH2F-CHF2 + CH2F = CH2F-CF2 + CH3F	1.00E+11	0.00	5033.	r CH3		nist	
31	CH2F-CF3 + CH2F = CF3-CHF + CH3F	2.00E+11	0.00	5033.	r CH3		nist	2
32	CHF2-CHF2 + CH2F = CHF2-CF2 + CH3F	3.00E+11	0.00	5536.	r CH3		nist	10
33	CHF2-CF3 + CH2F = CF3-CF2 + CH3F	2.00E+11	0.00	5033.	r CH3		nist	
34	CH3-CH2F + CHF2 = CH2F-CH2 + CH2F2	2.00E+11	0.00	6543.	r CH3		nist	
35	CH3-CH2F + CHF2 = CH3-CHF + CH2F2	1.50E+11	0.00	5033.	r CH3		nist	
36	CH3-CHF2 + CHF2 = CHF2-CH2 + CH2F2	2.00E+11	0.00	6039.	r CH3		nist	
37	CH3-CHF2 + CHF2 = CH3-CF2 + CH2F2	8.00E+10	0.00	5033.	r CH3		nist	
38	CH3-CF3 + CHF2 = CF3-CH2 + CH2F2	2.00E+11	0.00	6039.	r CH3		nist	
39	CH2F-CH2F + CHF2 = CH2F-CHF + CH2F2	3.00E+11	0.00	5033.	r CH3		nist	
40	CH2F-CHF2 + CHF2 = CHF2-CHF + CH2F2	2.00E+11	0.00	5033.	r CH3		nist	
41	CH2F-CHF2 + CHF2 = CH2F-CF2 + CH2F2	1.00E+11	0.00	5033.	r CH3		nist	
42	CH2F-CF3 + CHF2 = CF3-CHF + CH2F2	2.00E+11	0.00	5033.	r CH3		nist	
43	CHF2-CHF2 + CHF2 = CHF2-CF2 + CH2F2	3.00E+11	0.00	5033.	r CH3		nist	
44	CHF2-CF3 + CHF2 = CF3-CF2 + CH2F2	2.00E+11	0.00	5033.	r CH3		nist	
45	CH3-CH2F + CF3 = CH2F-CH2 + CHF3	9.50E+11	0.00	4127.	x			
46	CH3-CH2F + CF3 = CH3-CHF + CHF3	9.50E+11	0.00	4127.	x	71QUI/WHI		
47	CH3-CHF2 + CF3 = CHF2-CH2 + CHF3	3.10E+10	0.00	3573.	x	66OKS/PRA		
48	CH3-CHF2 + CF3 = CH3-CF2 + CHF3	3.10E+10	0.00	3573.	x	66OKS/PRA		
49	CH3-CF3 + CF3 = CF3-CH2 + CHF3	1.45E+12	0.00	6794.	x	67GIL/QUI		
50	CH2F-CH2F + CF3 = CH2F-CHF + CHF3	5.00E+11	0.00	3825.	r	nist		
51	CH2F-CHF2 + CF3 = CHF2-CHF + CHF3	3.00E+11	0.00	3624.	r	nist		
52	CH2F-CHF2 + CF3 = CH2F-CF2 + CHF3	2.00E+11	0.00	4026.	r	nist		
53	CH2F-CF3 + CF3 = CF3-CHF + CHF3	3.00E+11	0.00	3221.	r	nist		
54	CHF2-CHF2 + CF3 = CHF2-CF2 + CHF3	5.70E+11	0.00	5989.	x	67GIL/QUI		
55	CHF2-CF3 + CF3 = CF3-CF2 + CHF3	1.40E+11	0.00	5083.	x	67GIL/QUI		

GG	Fluoroethyls: Association with O2	A	b	E/R	note	refl	ref2	Hr
<i>1</i>	CH3-CHF + O2 = CH2:CHF + HO2	2.56E+19	-2.77	995.	r C2H5		nist	
<i>2</i>	CH3-CF2 + O2 = CH2:CF2 + HO2	2.56E+19	-2.77	995.	r C2H5		nist	
<i>3</i>	CH2F-CH2 + O2 = CH2:CHF + HO2	2.56E+19	-2.77	995.	r C2H5		nist	
<i>4</i>	CH2F-CHF + O2 = CHF:CHF-Z + HO2	2.56E+19	-2.77	995.	r C2H5		nist	
<i>5</i>	CH2F-CF2 + O2 = CHF:CF2 + HO2	2.56E+19	-2.77	995.	r C2H5		nist	
<i>6</i>	CHF2-CH2 + O2 = CH2:CF2 + HO2	2.56E+19	-2.77	995.	r C2H5		nist	
<i>7</i>	CHF2-CHF + O2 = CHF:CF2 + HO2	2.56E+19	-2.77	995.	r C2H5		nist	
<i>8</i>	CHF2-CF2 + O2 = CF2:CF2 + HO2	2.56E+19	-2.77	995.	r C2H5		nist	
<i>9</i>	CF3-CH2 + O2 = CF3 + CH2O + O	1.30E+13	0.00	22144.	r CF3		nist	
<i>10</i>	CF3-CHF + O2 = CF3 + CHF:O+O	1.30E+13	0.00	11575.	r CF3		nist	
<i>11</i>	CF3-CF2 + O2 = CF3 + CF2:O+O	1.30E+13	0.00	11575.	r CF3		nist	
Fluoroethyls: Association with O								
<i>12</i>	CH2F-CH2 + O = CH2O + CH2F	6.60E+13	0.00	0.	r C2H5	3A/3	nist	
<i>13</i>	CHF2-CH2 + O = CH2O + CHF2	6.60E+13	0.00	0.	r C2H5	3A/3	nist	
<i>14</i>	CF3-CH2 + O = CH2O + CF3	6.60E+13	0.00	0.	r C2H5	3A/3	nist	
<i>15</i>	CH3-CHF + O = CHF:O + CH3	4.40E+13	0.00	0.	r C2H5	2A/3	nist	
<i>16</i>	CH2F-CHF + O = CHF:O + CH2F	4.40E+13	0.00	0.	r C2H5	2A/3	nist	
<i>17</i>	CHF2-CHF + O = CHF:O + CHF2	4.40E+13	0.00	0.	r C2H5	2A/3	nist	
<i>18</i>	CF3-CHF + O = CHF:O + CF3	4.40E+13	0.00	0.	r C2H5	2A/3	nist	
<i>19</i>	CH3-CF2 + O = CF2:O + CH3	2.20E+13	0.00	0.	r C2H5	1A/3	nist	
<i>20</i>	CH2F-CF2 + O = CF2:O + CH2F	2.20E+13	0.00	0.	r C2H5	1A/3	nist	
<i>21</i>	CHF2-CF2 + O = CF2:O + CHF2	2.20E+13	0.00	0.	r C2H5	1A/3	nist	
<i>22</i>	CF3-CF2 + O = CF2:O + CF3	2.20E+13	0.00	0.	r C2H5	1A/3	nist	

Table 5 NIST HEC Mechanism

Table 5. NIST HFC Mechanism

GG	Fluoroethyls: Association with HO2		A	b	E/R	note	ref1	ref2	Hr
23	CH3-CHF + HO2	= CH3	+ CHF:O+OH	3.00E+13	0.00	0.	r C2H5	nist	nist
24	CH3-CF2 + HO2	= CH3	+ CF2:O+OH	3.00E+13	0.00	0.	r C2H5	nist	nist
25	CH2F-CH2 + HO2	= CH2F	+ CH2O+ OH	3.00E+13	0.00	0.	r C2H5	nist	nist
26	CH2F-CHF + HO2	= CH2F	+ CHF:O+OH	3.00E+13	0.00	0.	r C2H5	nist	nist
27	CH2F-CF2 + HO2	= CH2F	+ CF2:O+OH	3.00E+13	0.00	0.	r C2H5	nist	nist
28	CHF2-CH2 + HO2	= CHF2	+ CH2O+ OH	3.00E+13	0.00	0.	r C2H5	nist	nist
29	CHF2-CHF + HO2	= CHF2	+ CHF:O+OH	3.00E+13	0.00	0.	r C2H5	nist	nist
30	CHF2-CF2 + HO2	= CHF2	+ CF2:O+OH	3.00E+13	0.00	0.	r C2H5	nist	nist
31	CF3-CH2 + HO2	= CF3	+ CH2O+ OH	3.00E+13	0.00	0.	r C2H5	nist	nist
32	CF3-CHF + HO2	= CF3	+ CHF:O+OH	3.00E+13	0.00	0.	r C2H5	nist	nist
33	CF3-CF2 + HO2	= CF3	+ CF2:O+OH	3.00E+13	0.00	0.	r C2H5	nist	nist
34	CH3-CHF + HO2	= CH2:CHF	+ H2O2	3.00E+11	0.00	0.	r C2H5	2A/3	nist
35	CH3-CF2 + HO2	= CH2:CF2	+ H2O2	3.00E+11	0.00	0.	r C2H5	2A/3	nist
36	CH2F-CH2 + HO2	= CH2:CHF	+ H2O2	2.00E+11	0.00	0.	r C2H5	2A/3	nist
37	CH2F-CHF + HO2	= CHF:CHF-Z	+ H2O2	2.00E+11	0.00	0.	r C2H5	2A/3	nist
38	CH2F-CF2 + HO2	= CHF:CF2	+ H2O2	2.00E+11	0.00	0.	r C2H5	2A/3	nist
39	CHF2-CH2 + HO2	= CH2:CF2	+ H2O2	1.00E+11	0.00	0.	r C2H5	1A/3	nist
40	CHF2-CHF + HO2	= CHF:CF2	+ H2O2	1.00E+11	0.00	0.	r C2H5	1A/3	nist
41	CHF2-CF2 + HO2	= CF2:CF2	+ H2O2	1.00E+11	0.00	0.	r C2H5	1A/3	nist
42	CH3-CHF + HO2	= CH3-CH2F	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
43	CH3-CF2 + HO2	= CH3-CHF2	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
44	CH2F-CH2 + HO2	= CH3-CH2F	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
45	CH2F-CHF + HO2	= CH2F-CH2F	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
46	CH2F-CF2 + HO2	= CH2F-CHF2	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
47	CHF2-CH2 + HO2	= CH3-CHF2	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
48	CHF2-CHF + HO2	= CH2F-CHF2	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
49	CHF2-CF2 + HO2	= CHF2-CHF2	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
50	CF3-CH2 + HO2	= CH3-CF3	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
51	CF3-CHF + HO2	= CH2F-CF3	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist
52	CF3-CF2 + HO2	= CHF2-CF3	+ O2	3.00E+11	0.00	0.	r C2H5	nist	nist

JD	Fluoroethylenes: Thermal Decompositions	A	b	E/R	note	ref1	ref2	Hr
1	CH2:CHF	= C2H2 + HF	1.00E+14	0.00	35632. x	70SIM/QUI		
2	CH2:CF2	= C2HF + HF	2.50E+14	0.00	43281. x	70SIM/TSC		
3	CHF:CHF-Z	= C2HF + HF	2.50E+14	0.00	39255. r+dH			37
4	CHF:CF2	= C2F2 + HF	2.50E+14	0.00	50327. r+dH			37
	Fluoroethylenes: Activated Decomposition, Methylenе Combination (HF elimination)							
5	CH2SING + CHF	= C2H2 + HF	1.70E+20	-2.12	1198. r			
6	CH2SING + CF2	= C2HF + HF	1.70E+20	-2.12	1198. r			
7	CHF + CHF	= C2HF + HF	1.70E+20	-2.12	1198. r			
8	CHF + CF2	= C2F2 + HF	8.51E+19	-2.12	1198. k			
	Fluoroethylenes: Activated Decomposition, Methylenе Combination (stabilization)							
9	CH2SING + CHF	= CH2:CHF	3.10E+24	-3.80	1424. r			
10	CH2SING + CF2	= CH2:CF2	3.10E+24	-3.80	1424. r			
11	CHF + CHF	= CHF:CHF-Z	1.55E+24	-3.80	1424. r			
12	CHF + CF2	= CHF:CF2	3.10E+24	-3.80	1424. k			
13	CF2:CF2 + M	= CF2 + CF2 + M	3.96E+50	-9.06	42929. xk	78SCH/WAG		
	Fluoroethylenes: Activated Decomposition, Methylenе Combination (H atom elimination)							
14	CH2SING + CHF	= CH2:CF + H	1.64E+07	1.56	2889. r			
15	CH2SING + CHF	= CHF:CH-Z + H	3.28E+07	1.56	2889. r			
16	CH2SING + CF2	= CF2:CH + H	3.28E+07	1.56	2889. r			
17	CHF + CHF	= CHF:CF-Z + H	3.28E+07	1.56	2889. r			
18	CHF + CF2	= CF2:CF + H	1.64E+07	1.56	2889. k			
	Fluoroethylenes: Activated Decomposition, Vinyl + H (HF elimination)							
19	CH2:CF + H	= C2H2 + HF	5.98E+20	-2.31	976. r			
20	CHF:CH-Z + H	= C2H2 + HF	5.98E+20	-2.31	976. r			
21	CF2:CH + H	= C2HF + HF	5.98E+20	-2.31	976. r			
22	CHF:CF-Z + H	= C2HF + HF	5.98E+20	-2.31	976. r			
23	CF2:CF + H	= C2F2 + HF	5.98E+20	-2.31	976. k			
	Fluoroethylenes: Activated Decomposition, Vinyl + H (stabilization)							
24	CH2:CF + H	= CH2:CHF	2.40E+34	-7.11	2536. r			
25	CHF:CH-Z + H	= CH2:CHF	2.40E+34	-7.11	2536. r			
26	CF2:CH + H	= CH2:CF2	2.40E+34	-7.11	2536. r			
27	CHF:CF-Z + H	= CHF:CHF-Z	2.40E+34	-7.11	2536. r			
28	CF2:CF + H	= CHF:CF2	2.40E+34	-7.11	2536. k			

<i>J</i> A	Fluoroethylenes: H Atom Addition (stabilization)			<i>A</i>	<i>b</i>	E/R	note	ref1	ref2	Hr
<i>1</i>	CH2:CHF	+ H (+M)	= CH2F-CH2	(+M)	4.20E+08	1.50	498.	r C2H4	nist	
<i>2</i>	CH2:CHF	+ H (+M)	= CH3-CHF	(+M)	4.20E+08	1.50	498.	r C2H4	nist	
<i>3</i>	CH2:CF2	+ H (+M)	= CHF2-CH2	(+M)	4.20E+08	1.50	498.	r C2H4	nist	
<i>4</i>	CH2:CF2	+ H (+M)	= CH3-CF2	(+M)	4.20E+08	1.50	498.	r C2H4	nist	
	LOW/3.19E27	-2.8	-54./					r C2H4	nist	
	H2/2.0/ CO/2.0/	CO2/3.0	H2O/5.0/					r C2H4	nist	
<i>5</i>	CHF:CHF-Z	+ H (+M)	= CH2F-CHF	(+M)	8.40E+08	1.50	498.	r C2H4	nist	
	LOW/6.37E27	-2.8	-54./					r C2H4	nist	
	H2/2.0/ CO/2.0/	CO2/3.0	H2O/5.0/					r C2H4	nist	
<i>6</i>	CHF:CF2	+ H (+M)	= CHF2-CHF	(+M)	4.20E+08	1.50	498.	r C2H4	nist	
<i>7</i>	CHF:CF2	+ H (+M)	= CH2F-CF2	(+M)	4.20E+08	1.50	498.	r C2H4	nist	
	LOW/3.19E27	-2.8	-54./					r C2H4	nist	
	H2/2.0/ CO/2.0/	CO2/3.0	H2O/5.0/					r C2H4	nist	
<i>8</i>	CF2:CF2	+ H (+M)	= CHF2-CF2	(+M)	8.40E+08	1.50	498.	r C2H4	nist	
	LOW/6.37E27	-2.8	-54./					r C2H4	nist	
	H2/2.0/ CO/2.0/	CO2/3.0	H2O/5.0/					r C2H4	nist	
Fluoroethylenes: H Atom Addition (F atom displacement)										
<i>9</i>	C2H4	+ F	= CH2:CHF	+ H	2.00E+13	0.00	0.	ref		
<i>10</i>	CH2:CHF	+ F	= CH2:CF2	+ H	2.00E+12	0.00	0.	ref		
<i>11</i>	CH2:CHF	+ F	= CHF:CHF-Z	+ H	5.00E+12	0.00	0.	ref		
<i>12</i>	CHF:CHF-Z	+ F	= CHF:CF2	+ H	4.00E+12	0.00	0.	ref		
<i>13</i>	CHF:CF2	+ F	= CF2:CF2	+ H	2.00E+12	0.00	0.	ref		
Fluoroethylenes: H Atom Abstraction by H										
<i>14</i>	CH2:CHF	+ H	= CHF:CH-Z	+ H2	3.30E+05	2.53	6161.	rC2H4.	nist	
<i>15</i>	CH2:CHF	+ H	= CH2:CF	+ H2	3.30E+05	2.53	6161.	rC2H4	nist	
<i>16</i>	CH2:CF2	+ H	= CF2:CH	+ H2	6.70E+05	2.53	6161.	rC2H4	nist	
<i>17</i>	CHF:CHF-Z	+ H	= CHF:CF-Z	+ H2	3.30E+05	2.53	6161.	rC2H4	nist	
<i>18</i>	CHF:CF2	+ H	= CF2:CF	+ H2	3.30E+05	2.53	6161.	rC2H4	nist	

<i>J</i> O	Fluoroethylenes: Oxidation by O		A	b	E/R	note	ref1	ref2	Hr
<i>1</i>	CH2:CHF + O = CH2F + HCO		5.30E+09	1.00	659.	xf	87CVE	nist	
<i>2</i>	CHF:CHF-Z + O = CH2F + CF:O		7.00E+09	1.00	800.	xf	87CVE	nist	
<i>3</i>	CH2:CF2 + O = CHF2 + HCO		4.30E+09	1.00	750.	xf	87CVE	nist	
<i>4</i>	CHF:CF2 + O = CHF2 + CF:O		6.00E+09	1.00	579.	xf	87CVE	nist	
<i>5</i>	CF2:CF2 + O = CF2 + CF2:O		1.90E+09	1.00	0.	xf	87CVE	nist	
<i>6</i>	CH2:CHF + O = CH3 + CF:O		5.30E+09	1.00	1158.	ref E+1	74SLA/GUT	nist	
	Fluoroethylenes: H Atom Abstraction by OH								
<i>7</i>	CH2:CHF + OH = CHF:CH-Z + H2O		2.00E+06	2.00	1434.	xf	88TUL	nist	-6
<i>8</i>	CH2:CHF + OH = CH2:CF + H2O		1.00E+06	2.00	1434.	xf	88TUL	nist	-10
<i>9</i>	CHF:CHF-Z + OH = CHF:CF-Z + H2O		2.00E+06	2.00	1434.	xf	88TUL	nist	-5
<i>10</i>	CH2:CF2 + OH = CF2:CH + H2O		2.00E+06	2.00	1434.	xf	88TUL	nist	
<i>11</i>	CHF:CF2 + OH = CF2:CF + H2O		1.00E+06	2.00	1434.	xf	88TUL	nist	1

<i>J</i> O	Fluorovinyls: Oxidation by O <sub>2</sub>	A	b	E/R	note	ref1	Hr	ref2
<i>I2</i>	CH2:CF + O <sub>2</sub> = CH2O + CF:O	4.48E+26	-4.55	2758.	r C2H3	direct	nist	
<i>I3</i>	CHF:CH-Z + O <sub>2</sub> = CHF:O + HCO	4.48E+26	-4.55	2758.	r C2H3	direct	nist	
<i>I4</i>	CHF:CF-Z + O <sub>2</sub> = CHF:O + CF:O	4.48E+26	-4.55	2758.	r C2H3	direct	nist	
<i>I5</i>	CF2:CH + O <sub>2</sub> = CF2:O + HCO	4.48E+26	-4.55	2758.	r C2H3	direct	nist	
<i>I6</i>	CF2:CF + O <sub>2</sub> = CF2:O + CF:O	4.48E+26	-4.55	2758.	r C2H3	direct	nist	
<i>I7</i>	CH2:CF + O <sub>2</sub> = CH2O + CF:O	1.05E+38	-8.22	3538.	r C2H3	a/s	nist	
<i>I8</i>	CHF:CH-Z + O <sub>2</sub> = CHF:O + HCO	1.05E+38	-8.22	3538.	r C2H3	a/s	nist	
<i>I9</i>	CHF:CF-Z + O <sub>2</sub> = CHF:O + CF:O	1.05E+38	-8.22	3538.	r C2H3	a/s	nist	
<i>20</i>	CF2:CH + O <sub>2</sub> = CF2:O + HCO	1.05E+38	-8.22	3538.	r C2H3	a/s	nist	
<i>21</i>	CF2:CF + O <sub>2</sub> = CF2:O + CF:O	1.05E+38	-8.22	3538.	r C2H3	a/s	nist	
<b>Fluorovinyls: Oxidation by O</b>								
<i>22</i>	CH2:CF + O = CH2CO + F	3.00E+13	0.00	0.	r C2H3		nist	
<i>23</i>	CHF:CF-Z + O = CHFCO + F	3.00E+13	0.00	0.	r C2H3		nist	
<i>24</i>	CF2:CF + O = CF2CO + F	3.00E+13	0.00	0.	r C2H3		nist	
<i>25</i>	CHF:CH-Z + O = CHFCO + H	3.00E+13	0.00	0.	r C2H3		nist	
<i>26</i>	CF2:CH + O = CF2CO + H	3.00E+13	0.00	0.	r C2H3		nist	
<b>Fluorovinyls: Oxidation by OH</b>								
<i>27</i>	CH2:CF + OH = CH2CO + HF	3.00E+13	0.00	0.	r C2H3		nist	
<i>28</i>	CHF:CH-Z + OH = CHFCO + HF	3.00E+13	0.00	0.	r C2H3		nist	
<i>29</i>	CHF:CF-Z + OH = CHFCO + HF	2.00E+13	0.00	0.	r C2H3		nist	
<i>30</i>	CF2:CF + OH = CF2CO + HF	1.00E+13	0.00	0.	r C2H3		nist	
<i>31</i>	CH2:CF + OH = CH3 + CF:O	3.00E+13	0.00	0.	r C2H3		nist	
<i>32</i>	CHF:CH-Z + OH = CH2F + HCO	3.00E+13	0.00	0.	r C2H3		nist	
<i>33</i>	CHF:CF-Z + OH = CH2F + CF:O	4.00E+13	0.00	0.	r C2H3		nist	
<i>34</i>	CF2:CF + OH = CHF2 + CF:O	5.00E+13	0.00	0.	r C2H3		nist	

KK	Fluoroethynes: H Atom Addition/Stabilization			A	b	E/R	note	ref1	ref2	Hr
<i>1</i>	C2HF	+ H (+M)	= CH2:CF	(+M)	2.80E+12	0.00	1213.	rC2H2		nist
<i>2</i>	C2HF	+ H (+M)	= CHF:CH-Z	(+M)	1.40E+12	0.00	1213.	rC2H2		nist
<i>3</i>	LOW/0.67E27	-3.5	2410./							
	H2/2./	CO2/2./	CO2/3./	H2O/5./						
<i>4</i>	C2F2	+ H (+M)	= CHF:CF-Z	(+M)	2.80E+12	0.00	1213.	rC2H2		nist
	LOW/1.33E27	-3.5	2410./							
	H2/2./	CO2/2./	CO2/3./	H2O/5./						
Fluoroethynes: Oxidation										
<i>5</i>	C2HF	+ O	= FCCO-E	+ H	1.00E+07	2.00	956.	rC2H2 x2	MB A077	nist
<i>6</i>	C2F2	+ O	= FCCO-E	+ F	1.00E+07	2.00	956.	rC2H2 x2	MB A077.	nist
<i>7</i>	C2HF	+ OH	= CHFCO	+ H	2.18E-04	4.50	-503.	rC2H2 x2	MB A089	nist
<i>8</i>	C2HF	+ OH	= CH2F	+ CO	2.50E-04	4.00	-1007.	rC2H2 /2	MB A090	nist
<i>9</i>	C2HF	+ OH	= HCCO	+ HF	2.50E-04	4.00	-1007.	rC2H2 /2	MB A090	nist
<i>10</i>	C2F2	+ OH	= CF2CO	+ H	2.18E-04	4.50	-503.	r C2H2	MB A089	nist
<i>11</i>	C2F2	+ OH	= FCCO-E	+ HF	2.50E-04	4.00	-1007.	r C2H2	MB A090	nist
Fluoroketenes, Fluoroketyl										
<i>12</i>	CHFCO	+ H	= CH2F	+ CO	1.13E+13	0.00	1725.	r CH2CO	MB A094	nist
<i>13</i>	CF2CO	+ H	= CHF2	+ CO	1.13E+13	0.00	1725.	r CH2CO	MB A094	nist
<i>14</i>	CHFCO	+ H	= FCCO-E	+ H2	5.00E+13	0.00	4026.	r CH2CO	MB A095	nist
<i>15</i>	CHFCO	+ O	= CHF:O	+ CO	1.00E+13	0.00	4026.	ul		nist
<i>16</i>	CF2CO	+ O	= CF2:O	+ CO	1.00E+13	0.00	4026.	ul		nist
<i>17</i>	CHFCO	+ OH	= FCCO-E	+ H2O	7.50E+12	0.00	1007.	r CH2CO	MB A097	nist
<i>18</i>	FCCO-E	+ H	= CHF	+ CO	1.00E+14	0.00	0.	r HCCO	MB A101	nist
<i>19</i>	FCCO-E	+ O	= CF:O	+ CO	1.00E+14	0.00	0.	r HCCO	MB A102	nist

Table 5. NIST HFC Mechanism

<i>CF</i>	F Atom Reactions	<i>A</i>	<i>b</i>	E/R	note	ref1	ref2	Hr
<i>1</i> CH4	+ F	= CH3	+ HF	5.90E+12	0.50	226. xf	92ATK/BAU	-31
<i>2</i> CH3F	+ F	= CH2F	+ HF	1.35E+14	0.00	604. xf	83MAN/SET	-37
<i>3</i> CH2F2	+ F	= CHF2	+ HF	9.00E+13	0.00	931. xf	85CLY/HOD	-36
<i>4</i> CHF3	+ F	= CF3	+ HF	4.50E+13	0.00	1862. xf	83CLY/HOD	-27
<i>5</i> CH3OH	+ F	= CH3O	+ HF	2.62E+09	1.44	-103. x	91GLA/KOS	
<i>6</i> CH3OH	+ F	= CH2OH	+ HF	4.62E+07	1.97	-151. x	91GLA/KOS	
<i>7</i> CH2O	+ F	= HCO	+ HF	6.00E+13	0.00	1007. r CHFO	90FRA/ZHA	-45
<i>8</i> CHFO:O	+ F	= CF:O	+ HF	2.65E+13	0.00	906. x	90FRA/ZHA	-35
<i>9</i> CH3O	+ F	= CH2O	+ HF	3.00E+13	0.00	0. ul	nist	-114
<i>10</i> HCO	+ F	= CO	+ HF	1.00E+13	0.00	0. ul	nist	-120
<i>11</i> C2H6	+ F	= C2H5	+ HF	8.00E+12	0.00	151. x	60FET/KNO	
<i>12</i> CH3-CH2F	+ F	= CH2F-CH2	+ HF	9.00E+13	0.00	403. r C2H6	nist	
<i>13</i> CH3-CHF2	+ F	= CHF2-CH2	+ HF	1.00E+14	0.00	403. r C2H6	nist	
<i>14</i> CH3-CF3	+ F	= CF3-CH2	+ HF	1.00E+14	0.00	2013. r C2H6	nist	
<i>15</i> CH3-CH2F	+ F	= CH3-CHF	+ HF	6.00E+13	0.00	101. r C2H6	nist	
<i>16</i> CH2F-CH2F	+ F	= CH2F-CHF	+ HF	1.30E+14	0.00	403. r C2H6	nist	
<i>17</i> CH2F-CHF2	+ F	= CHF2-CHF	+ HF	1.30E+14	0.00	403. r C2H6	nist	
<i>18</i> CH2F-CF3	+ F	= CF3-CHF	+ HF	6.00E+13	0.00	604. r C2H6	nist	
<i>19</i> CH3-CHF2	+ F	= CH3-CF2	+ HF	3.00E+13	0.00	403. r C2H6	nist	
<i>20</i> CH2F-CHF2	+ F	= CH2F-CF2	+ HF	3.00E+13	0.00	604. r C2H6	nist	
<i>21</i> CHF2-CHF2	+ F	= CHF2-CF2	+ HF	6.00E+13	0.00	604. r C2H6	nist	
<i>22</i> CHF2-CF3	+ F	= CF3-CF2	+ HF	4.00E+13	0.00	705. r C2H6	nist	
<i>23</i> C2H4	+ F	= C2H3	+ HF	1.00E+14	0.00	1007. r CH4	nist	-33
<i>24</i> CF2:CF2	+ F	= CF3	+ CF2	3.00E+13	0.00	0. r H	nist	-34
<i>25</i> C2H3	+ F	= C2H2	+ HF	2.00E+13	0.00	0. r H	nist	-18

REF	REFERENCE	REACTIONS (H,F,O)	A	b	E/R	note	refI	refII	Hr
1	HF	+ M = H + F	3.12E+13	0.00	49985.	x	81BAU/DUX	3000-5000K?	
2	H2	+ F = H + HF	7.23E+13	0.00	470.	x	89STE/BRU	221-376K	
3	HO2	+ F = O2 + HF	5.00E+13			x	83WAL/WAG	300K	
4	H2O	+ F = OH + HF	2.53E+13	0.00	400.	x	83WAL/WAG	243-369K	
5	H2O2	+ F = HO2 + HF	3.00E+13			x	83WAL/WAG	300K	
REFERENCE REACTIONS (Fluoromethane: Decomposition)									
6	CH3F	= CH2SING + HF	1.00E+14	0.00	42778.	x	79SCH/WAG	1150-1570K	
7	CH3F	+ M = CH2SING + HF	1.00E+16	0.00	33971.	x	79SCH/WAG	1150-1570K	
8	CH2F2	= CHF + HF	8.90E+12	0.00	35380.	x	68POL/SHE	1060-1320K	
9	CHF3	+ M = CF2 + HF	1.30E+16	0.00	29391.	x	91HID/NAK	1500-2500K	
10	CF3	+ F = CF4 + HF	7.80E+12			x	86PLU/PYA	295K	
11	CF3	+ H = CF2 + HF	5.48E+13			x	89TSA/MCF	298K	
REFERENCE REACTIONS (Fluoromethane: Abstraction, Metathesis)									
12	CH3F	+ H = CH2F + H2	1.80E+13	0.00	4731.	x	75WES/DEH	605-871K	
13	CH2F2	+ H = CHF2 + H2	1.32E+13	0.00	4731.	x	72RID/DAV	873-953K	
14	CHF3	+ H = CF3 + H2	3.32E+13	0.00	55336.	xrev	78ART/BEL	350-600K	
15	CF3	+ H2 = CHF3 + H	8.90E+11	0.00	4781.	x	78ART/BEL	350-600K	
16	CH3F	+ O = CH2F + OH	7.83E+12	0.00	4882.	x	67PAR/AZA	858-933K	
17	CH2F2	+ O = CHF2 + OH	2.65E+12	0.00	4429.	x	68PAR/NAL	873-953K	
18	CHF3	+ O = CF3 + OH	5.00E+12	0.00	5385.	x	78JOU/LEB	390-620K	
19	CH4	+ F = CH3 + HF	1.80E+14	0.00	403.	xv	92ATK/BAU	250-450K	
20	CH3F	+ F = CH2F + HF	0.34 CH4+			x	83MAN/SET	300K	
21	CH2F2	+ F = CHF2 + HF	3.40E+12			x	85CLY/HOD	298K	
22	CHF3	+ F = CF3 + HF	9.00E+10			x	83CLY/HOD	298K	
23	CH3F	+ OH = CH2F + H2O	4.90E+12	0.00	1887.	x	82JEO/KAU	292-480K	
24	CH2F2	+ OH = CHF2 + H2O	2.65E+12	0.00	1772.	x	82JEO/KAU	250-492K	
25	CHF3	+ OH = CF3 + H2O	1.80E+12	0.00	2914.	x	82JEO/KAU	387-480K	
26	CH3	+ H2O2 = CH4 + HO2	1.21E+10	0.00	-300.	xv	86TSA/HAM		
27	CH2O	+ CH3 = HCO + CH4	5.54E+03	2.81	2950.	xv	86TSA/HAM		
28	CH3OH	+ CH3 = CH3O + CH4	1.44E+01	3.10	3490.	xv	86TSA/HAM		
29	CH3OH	+ CH3 = CH2OH + CH4	3.20E+01	3.20	3608.	xv	87TSA		
30	HCO	+ CH3 = CO + CH4	1.20E+14	0.00	0.	xv	86TSA/HAM		

Table 5. NIST HFC Mechanism

REF	REFERENCE	REACTIONS (Fluoromethyl Oxidation)	A	b	E/R	note	ref1	ref2	Hr
31	CH3	+ O = CH2O + H	8.43E+13	0.00	0.	xv	92BAU/COB		
32	CH3	+ OH = Products	3.61E+13	0.00	0.	xv	92BAU/COB		
33	CH3	+ HO2 = CH3O + OH	1.81E+13	0.00	0.	v	92BAU/COB		
34	CH3	+ HO2 = CH4 + O2	3.61E+12	0.00	0.	v	86TSA/HAM		
35	CF3	+ O = CF2:O + F	1.87E+13	x	x		89TSA/BEL	293K	
36	REFERENCE	REACTIONS (Fluoromethylene, Fluoromethylidyne Oxidation, Destruction)							
36	CF2	+ F2 = CF3 + F	5.00E+10		x		82SEE/ROT	550K	
37	CF2	+ F2 = CF3 + F	1.20E+09		xul		86PLU/RYA	295K	
38	CF2	+ O = PRODUCTS	1.21E+13		x		90TSA/MCF	293K	
39	CF2	+ OH = CF2:O + H	5.00E+12		x		78BIO/LAZ	1090-1375K	
38	CH	+ O2 = PRODUCTS	3.30E+13	0.00	0.	xv	92BAU/COB		
39	CH	+ H2O = PRODUCTS	5.70E+12	0.00	-382.	xv	92BAU/COB		
40	CF	+ H = PRODUCTS	1.15E+13		x		89TSA/MCF	298K	
41	CF	+ O = PRODUCTS	7.23E+12		x		90TSA/MCF	293K	
42	CF	+ O2 = PRODUCTS	9.64E+11		x		92PEE/VAN	294K	
43	REFERENCE	REACTIONS (Carbonyl Fluorides)							
43	CHF:O	+ M = CO + HF	2.48E+25	-3.00	21641.	xg	85SAU/KUR	nist	-2
44	CHF:O	+ H = CF:O + H2	1.10E+08	1.77	1510.	r CH2O	A/2	nist	-4
45	CHF:O	+ O = CF:O + OH	9.00E+12	0.00	1550.	r CH2O		nist	-2
46	CHF:O	+ OH = CF:O + H2O	1.72E+09	1.18	2225.	r CH2O		nist	-18
47	CF:O	+ H2O2 = CHF:O + HO2	1.00E+11	0.00	1963.	r	E*0.56	nist	-13
48	CHF:O	+ CH3 = CF:O + CH4	2.00E+12	0.00	4529.	rul		nist	-4
49	CF:O	+ H = CO + HF	1.20E+14	0.00	0.	r HCO		nist	-102
50	CF:O	+ O = CO2 + F	3.00E+13	0.00	0.	r HCO		nist	-94
51	CF:O	+ OH = CO2 + HF	3.00E+13	0.00	0.	r HCO		nist	-128
52	CF:O	+ HO2 = CO2 + F + OH	3.00E+13	0.00	0.	r HCO		nist	-28
53	REFERENCE	REACTIONS (Fluoroethanes, Fluoroethyls: Carbene Insertion into Fluoromethanes, Fluoromethyls)							
53	CH3F	+ CH2SING = C2H4 + HF	4.00E+13	0.00	0.	r			
54	CH2F	+ CH2 = CH2:CHF + H	4.00E+13	0.00	0.	r CH3			
55	REFERENCE	REACTIONS (Fluoroethanes: H Atom Abstraction by H, O, OH)							
55	CH3-CH2F	+ OH = CH2F-CH2 + H2O	5.50E+07	1.60	550.	rxt	91COH/WES	nist	-101
56	CH3-CH2F	+ OH = CH3-CHF + H2O	3.30E+07	1.60	550.	rxt	91COH/WES	nist	-66
57	CH3-CHF2	+ OH = CHF2-CH2 + H2O	1.54E+07	1.60	570.	rxt	91COH/WES		-13
58	CH3-CHF2	+ OH = CH3-CF2 + H2O	4.40E+06	1.60	670.	rxt	91COH/WES		
59	CH2F-CHF2	+ OH = CHF2-CHF + H2O	2.05E+07	1.70	906.	rxt	87COH/BEN		
60	CH2F-CHF2	+ OH = CH2F-CF2 + H2O	1.06E+07	1.70	1510.	rxt	87COH/BEN		

Table 5. NIST HFC Mechanism

REF	REFERENCE REACTIONS (Fluoroethanes: H Atom Abstraction by CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> , C <sub>2</sub> H <sub>3</sub> , HCO)	ref1	ref2	Hr
61	CH <sub>3</sub> -CH <sub>2</sub> F + CH <sub>3</sub> = CH <sub>2</sub> F-CH <sub>2</sub> + CH <sub>4</sub>	2.00E+11	0.00	6744.
62	CH <sub>3</sub> -CH <sub>2</sub> O + CH <sub>2</sub> O = CH <sub>3</sub> -CH <sub>2</sub> F + HCO	5.50E+03	2.80	2969. r C <sub>2</sub> H <sub>5</sub>
<b>REFERENCE REACTIONS (Fluoroethanes, Fluoroethyls: Association with O<sub>2</sub>, O, HO<sub>2</sub>)</b>				
63	CH <sub>3</sub> -CHF + H <sub>2</sub> O <sub>2</sub> = CH <sub>3</sub> -CH <sub>2</sub> F + HO <sub>2</sub>	9.00E+09	0.00	503. r C <sub>2</sub> H <sub>5</sub>
64	CH <sub>3</sub> -CHF + O <sub>2</sub> = CH <sub>2</sub> ·CHF + HO <sub>2</sub>	2.56E+19	-2.77	995. r C <sub>2</sub> H <sub>5</sub>
65	CH <sub>2</sub> F-CH <sub>2</sub> + O = CH <sub>2</sub> O + CH <sub>2</sub> F	6.60E+13	0.00	0. r C <sub>2</sub> H <sub>5</sub> 3A/3
66	CH <sub>3</sub> -CHF + HO <sub>2</sub> = CH <sub>2</sub> ·CHF + H <sub>2</sub> O <sub>2</sub>	3.00E+11	0.00	0. r C <sub>2</sub> H <sub>5</sub> 2A/3
<b>REFERENCE REACTIONS (Fluoroethylenes: H Atom Addition/Stabilization, F Atom Displacement, H Atom Abstraction)</b>				
67	CH <sub>2</sub> .CF <sub>2</sub> + H (+M) = CH <sub>3</sub> -CF <sub>2</sub> (+M)	4.20E+08	1.50	498. r C <sub>2</sub> H <sub>4</sub> r C <sub>2</sub> H <sub>4</sub>
	LOW/3.19E27 -2.8 -54./			
C2H4	+ F = CH <sub>2</sub> :CHF + H	2.00E+13	0.00	0. ref
68	CH <sub>2</sub> .CHF + H = CHF:CH-Z + H <sub>2</sub>	3.30E+05	2.53	6161. rC2H4
<b>REFERENCE REACTIONS (Fluoroethylenes: Oxidation by O<sub>2</sub>)</b>				
69	CH <sub>2</sub> .CHF + O = CH <sub>2</sub> F + HCO	5.30E+09	1.00	659. xf
70	CHF:CHF-Z + O = CH <sub>2</sub> F + CF:O	7.00E+09	1.00	800. xf
71	CH <sub>2</sub> .CF <sub>2</sub> + O = CHF <sub>2</sub> + HCO	4.30E+09	1.00	750. xf
72	CHF:CF <sub>2</sub> + O = CHF <sub>2</sub> + CF:O	6.00E+09	1.00	579. xf
73	CF <sub>2</sub> .CF <sub>2</sub> + O = CF <sub>2</sub> + CF <sub>2</sub> :O	1.90E+09	1.00	0. xf
<b>REFERENCE REACTIONS (Fluoroethylenes: H Atom Abstraction by OH)</b>				
74	CH <sub>2</sub> .CHF + OH = CHF:CH-Z + H <sub>2</sub> O	2.00E+06	2.00	1434. xf
				88TUL nist
<b>REFERENCE REACTIONS (Fluorovinyls)</b>				
75	CH <sub>2</sub> .CF + O <sub>2</sub> = CH <sub>2</sub> O + CF:O	4.48E+26	-4.55	2758. r C <sub>2</sub> H <sub>3</sub>
76	CH <sub>2</sub> .CF + O <sub>2</sub> = CH <sub>2</sub> O + CF:O	1.05E+38	-8.22	3538. r C <sub>2</sub> H <sub>3</sub> direct a/s
77	CH <sub>2</sub> .CF + O = CH <sub>2</sub> CO + F	3.00E+13	0.00	0. r C <sub>2</sub> H <sub>3</sub>
78	CH <sub>2</sub> .CF + OH = CH <sub>2</sub> CO + HF	3.00E+13	0.00	0. r C <sub>2</sub> H <sub>3</sub>
<b>REFERENCE REACTIONS (Fluoroethynes)</b>				
79	C <sub>2</sub> HF + H (+M) = CHF:CH-Z (+M)	1.40E+12	0.00	1213. rC2H2
	LOW/0.67E27 -3.5 2410./			nist
H2/2./	CO/2./ CO <sub>2</sub> /3./ H <sub>2</sub> O/5./			
80	C2HF + O = FCCO-E + H	1.00E+07	2.00	956. rC2H2 x2 MB A077
81	C2HF + OH = CHFCO + H	2.18E-04	4.50	-503. rC2H2 x2 MB A089
82	C2HF + OH = CH2F + CO	2.50E-04	4.00	-1007. rC2H2 /2 MB A090

Table 5. NIST HFC Mechanism

REF	REFERENCE REACTIONS (Fluoroketenes, Fluoroketyl)	A	b	E/R	note	ref1	ref2	Hr
83	CHFCO + H = CH2F + CO	1.13E+13	0.00	1725.	r CH2CO	MB A094	nist	
84	CHFCO + H = FCCO-E + H2	5.00E+13	0.00	4026.	r CH2CO	MB A095	nist	
85	CHFCO + OH = FCCO-E + H2O	7.50E+12	0.00	1007.	r CH2CO	MB A097	nist	
86	FCCO-E + H = CHF + CO	1.00E+14	0.00	0.	r HCCO	MB A101	nist	
87	FCCO-E + O = CF;O + CO	1.00E+14	0.00	0.	r HCCO	MB A102	nist	
	REFERENCE REACTIONS(F Atom Reactions)							
88	CH2O + F = HCO + HF	6.00E+13	0.00	1007.	r CHFO		nist	-45
89	C2H3 + F = C2H2 + HF	2.00E+13	0.00	0.	r C2H3		nist	
90	CHF:CF-Z + F = CHF + CF2	1.00E+13	0.00	0.	r C2H3		nist	
91	CF2:CF2 + F = CF3 + CF2	3.00E+13	0.00	0.	r C2H3		nist	-18

NOTE	EXPLANATION
k	$AT^b e^{-E/RT}$
A	prefactor (mol, cm <sup>3</sup> , s <sup>-1</sup> )
b	temperature dependence (dimensionless)
E/R	activation energy (K)
Hr	heat of reaction (kcal/mol)
x	experimental data
xh	experimental data measured at high temperatures
xf	experimental data fit with reasonable temperature dependence (b)
xg	experimental data fit with temperature dependence
xt	experimental data fit with TST temperature dependence
xk	RRKM benchmarked to experimental data
xv	evaluated recommendation based on experimental data
xrev	based on experimental data for reverse reaction
r	relative to reference reaction (e.g., r CH3 - referenced to analogous reaction for CH3)
rul	relative to reference reaction, upper limit estimate
ul	upper limit estimate
k	RRKM
a	calculated with ab initio transition state partition functions
ak	RRKM with ab initio thermodynamics

NOTATION	REFERENCE
65PRI/BRY	Pritchard et al., 1965
65TSC	Tschuikow-Roux, 1965
67PAR/AZA	Parsamyan et al., 1970
68PAR/NAL	Parsamyan and Nalbandyan, 1968
70CAD/DAY	Cadman et al., 1970
70SIM/QUI	Simmie et al., 1970
70TSC/QUI	Tschuikow-Roux and Quiring, 1970
71BRA/BEL	Brabbs et al., 1971
71JAC/HOU	Jachimowski and Houghton, 1971
71KER/TIM	Kerr and Timlin, 1971
71KOC/MOI	Kochubei and Moin, 1971
71MIL/HAR	Millward et al., 1971
71TSC/MIL	Tschuikow-Roux et al., 1971a
71TSC/QUI	Tschuikow-Roux et al., 1971b
71WAG/WAR	Wagner et al., 1971
72KER/PAR	Kerr and Parsonage, 1972
72MIL/TSC	Millward and Tschuikow-Roux, 1972
72RID/DAV	Ridley et al., 1972
72SKI/LIF	Skinner et al., 1972
73CLA/DOV	Clark and Dove, 1973
73PPE/MAH	Peeters and Mahnen, 1973
73SCH/WAG	Schug and Wagner, 1973
74SEK/TSC	Sekhar and Tschuikow-Roux, 1974
74SLA/GUT	Slage et al., 1974
75BOW	Bowman, 1975
75WES/DEH	Westenberg and deHaas, 1975
76PAY/STI	Payne and Stieff, 1976
77ATR/BAL	Atri et al., 1977
77KEA/MAT	Keating and Matula, 1977
78ART/BEL	Arthur and Bell, 1978
78BIO/LAZ	Biordi et al., 1978
78JOU/LEB	Jourdain et al., 1978
79COH/WES	Cohen and Westberg, 1979
79MIC/NAV	Michael et al., 1979
79SCH/WAG	Schug et al., 1979

Table 5. NIST HFC Mechanism

Table 5. NIST HFC Mechanism

NOTATION	REFERENCE
80BUT/FLE	Butler et al., 1980
80DEA/JOH	Dean et al., 1980
80KLE/SKO	Klemm et al., 1980
81BAU/DUX	Baulch et al., 1981
81HOW/SMI	Howard and Smith, 1981
81MES/FIL	Messing et al., 1981
81VEY/LES	Veyret and Lesclaus, 1981
82BER/FLE	Berman et al., 1982
83BAU/CRA	Baulch et al., 1983
83KIE/KAP	Kiefer et al., 1983
83TUL/RAV	Tully et al., 1983
83WAL/WAG	Walther and Wagner, 1983
83WAS/HAT	Washida et al., 1983
84RYA/PLU	Ryan and Plumb, 1984
84TEM/WAG	Temps and Wagner, 1984
84WAR	Warnatz, 1984
85SAI/KUR	Saito et al., 1985
86PLU/RYA	Plumb and Ryan, 1986a, 1986b
86SUT/MIC	Sutherland et al., 1986
86TSA/HAM	Tsang and Hampson, 1986
87COH/BEN	Cohen and Benson, 1987a, 1987b
87CVE	Cvetanovic, 1987
87DEA/WES	Dean and Westmoreland, 1987
88SUT/MIC	Sutherland et al., 1988
88WAG/WAR	Wagner and Wardlaw, 1988
88ZAB/FLE	Zabarnick et al., 1988
89STE/BRU	Stevens et al., 1989
89STE/SMI	Steward, P.H.
89TSA/BEL	Tsai et al., 1989
89TSA/MCF	Tsai and McFadden, 1989

Table 5. NIST HFC Mechanism

NOTATION	REFERENCE
90BOZ/DEA	Bozzelli and Dean, 1990
90NOR	Norton, 1990
90TSA/MCF	Tsai and McFadden, 1990a, 1990b
91COH/WES	Cohen and Westberg, 1991
91HD/NAK	Hidaka et al., 1991
92BAU/COB	Baulch et al., 1992
92MARSZE	Maricq and Szente, 1992
92WES	Westmoreland, 1992
RRKM	this work, RRKM calculations
QRRK	this work, QRRK calculations
BAC	this work, BAC-MP4 & RRKM calculations
ref	this work, by analogy to other reactions



## **6. Bibliography**

### **6.1. Overview**

A list of references is given below that was compiled and reviewed as part of this work.

The list of references is divided into a number of different sections:

- (6.2) General Thermochemistry and Kinetics,
- (6.3) Hydrocarbon Chemistry,
- (6.4) Fluorine Chemistry,
- (6.5) Fluorocarbon Thermochemistry,
- (6.6) Oxidized Fluorocarbon Thermochemistry,
- (6.7) Fluorocarbon Kinetics (Decompositions),
- (6.8) Fluorocarbon Kinetics (Abstractions),
- (6.9) Fluorocarbon Kinetics (Oxidations),
- (6.10) Oxidized Fluorocarbon Kinetics,
- (6.11) Fluorocarbon Kinetics (Other),
- (6.12) Flame Inhibition (Halogens), and
- (6.13) Flame Inhibition (non-Halogens).

The references for "Hydrocarbon Kinetics" are not meant to be comprehensive, but rather documentation of those rate constants used in this work. The references for "Flame Inhibition" are also not meant to be comprehensive, but rather representative of flame inhibition chemistry as related to this work. In the other reference sections, all relevant references are included, both those references for which thermochemical or kinetic data were utilized in the reaction set, as well as other related sources of relevant data.



## 6.2. General Thermochemistry and Kinetics

Authors	Journal	Issue	Pages	Year	Title
Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Jr., Kerr, J.A., and Troe, J.,	<i>J. Phys. Chem. Ref. Data</i>	21,	1125-1568	(1992).	<i>Evaluated kinetic and photochemical data for atmospheric chemistry. Supplement IV. IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry,</i>
Baulch, D.L., Cobos, C.J., Cox, R.A., Esser, C., Frank, P., Just, Th., Kerr, J.A., Pilling, M.J., Troe, J., Walker, R.W., and Warnatz, J.,	<i>J. Phys. Chem. Ref. Data</i>	21,	411-429	(1992).	<i>Evaluated kinetic data for combustion modeling,</i>
Baulch, D.L., Duxbury, J., Grant, S.J., and Montague, D.C.,	<i>J. Phys. Chem. Ref. Data</i>	10,	Suppl. 1	(1981).	<i>Evaluated kinetic data for high temperature reactions. Volume 4 Homogeneous gas phase reactions of halogen- and cyanide-containing species,</i>
Benson, S.W.,	<i>Thermochemical Kinetics</i> , Wiley, New York, NY, 1976.				
Bowman, C.T., Frenklach, M., Gardiner, W., Golden, D., Lissianski, V., Smith, G., and Wang, Burke, S.P. and Schumann, T.E.W.,	<i>Gas Research Institute Report, 1995</i>				<i>GRIMECH (in preparation)</i>
Cohen, N. and Westberg, K.,	<i>Ind. Eng. Chem.</i>	20,	998	(1928).	
Cohen, N. and Westberg, K.R.,	<i>J. Phys. Chem.</i>	83,	46	(1979).	<i>Evaluation and Compilation of Chemical Kinetic Data,</i>
Cohen, N. and Westberg, K.R.,	<i>J. Phys. Chem. Ref. Data</i>	12,	531	(1983).	<i>Chemical kinetic data sheets for high-temperature chemical reactions,</i>
Cohen, N. and Westberg, K.R.,	<i>J. Phys. Chem. Ref. Data</i>	20,	1211-1311	(1991).	<i>Chemical Kinetic data sheets for high-temperature reactions. Part II,</i>
Curtiss, L.A., Raghavachari, K., Trucks, G.W., and Pople, J.A.,	<i>J. Chem. Phys.</i>	94,	7221-7230	(1991).	<i>Gaussian-2 Theory for Molecular Energies of First- and Second-Row Compounds,</i>
Cvetanovic, R.J., Singleton, D.L., and Paraskevopoulos, G.,	<i>J. Phys. Chem.</i>	83,	50	(1979).	<i>Evaluations of the mean values and standard errors of rate constants and their temperature coefficients,</i>
Daubert, T.E. and Danner, R.P.,	<i>NIST Standard Reference Database</i>	11,		(1985).	<i>DIPPR Data Compilation of Pure Compound Properties,</i>
Dean, A.M. and Westmoreland, P.R.,	<i>Inter. J. Chem. Kin.</i>	19,	207-228	(1987).	<i>Bimolecular QRRK analysis of methyl radical reactions,</i>
Egolfopoulos, F.N., Du, D.X., and Law, C.K.,	<i>Combust. Sci. Technol.</i>	83,	33-75	(1992).	<i>A comprehensive study of methanol kinetics in flame-propagating and burner-stabilized flames, flow and static reactors, and shock tubes,</i>
Egolfopoulos, F.N., Zhu, D.L., and Law, C.K.,	<i>Symp. Int. Combust.</i>	23,	471-478	(1990).	<i>Experimental and numerical determination of laminar flame speeds: mixtures of C2-hydrocarbons with oxygen and nitrogen,</i>
Frisch, M.J., Trucks, G.W., Head-Gordon, M., Gill, P.M.W., Wong, M.W., Foresman, J.B., Johnson, B.G., Schlegel, H.B., Robb, M.A., Repogle, E.S., Gomperts, R., Andres, J.L., Raghavachari, K., Binkley, J.S., Gonzalez, C., Glarborg, P., Miller, J.A., and Kee, R.J.,	<i>Gaussian, Inc., Pittsburgh, PA, 1992</i>				<i>Gaussian 92</i>
Hart, L.W., Grunfelder, C., and Fristrom, R.M.,	<i>Combust. Flame</i>	65,	177-202	(1986).	<i>Kinetic modeling and sensitivity analysis of nitrogen oxide formation in well-stirred reactors,</i>
	<i>Combust. Flame</i>	23,	109-119	(1974).	<i>The 'point source' technique using upstream sampling for rate constant determinations in flame gases,</i>

## 6.2. General Thermochemistry and Kinetics

Authors	Journal	Issue	Pages	Year	Title
Hunter, T.B., Wang, H., Litzinger, T.A., and Frenklach, M.,	<i>Combust. Flame</i>	97,	201-224	(1994).	<i>The oxidation of methane at elevated pressure: experiments and modeling,</i>
Kee, R.J., Grcar, J.F., Smooke, M.D., and Miller, J.A.,	SAND85-8240, Sandia National Laboratories,			(1985).	<i>A Fortran Program for Modeling Steady Laminar One-Dimensional Premixed Flames,</i>
Kee, R.J., Miller, J.A., and Jefferson, T.H.,	SAND80-8003, Sandia National Laboratories,			(1980).	<i>CHEMKIN: A General-Purpose, Problem Independent, Transportable, Fortran Chemical Kinetics Code Package,</i>
Kee, R.J., Miller, J.A., and Jefferson, T.H.,	SAND80-8003, Sandia National Labs, 1989				<i>CHEMKIN: A General-Purpose, Problem Independent, Transportable, Fortran Chemical Kinetics Code Package,</i>
Kee, R.J., Rupley, F.M., and Miller, J.A.,	SAND87-8215B, Sandia National Labs, 1987				<i>The CHEMKIN Thermodynamic Database,</i>
Kerr, J.A., and Parsonage, M.J.,	<i>Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds</i> , Butterworths, London, 1972.				
Kerr, J.A., and Parsonsage, M.J.,	<i>Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals, Butterworths, London, 1976.</i>				
Kondratenko, V.N.,	NBS COM-72-10014,			(1974).	<i>Rate Constants of Gas Phase Reactions,</i>
Mallard, W.G., Westley, F., Herron, J.T., Hampson, R.F., and Frizzell, D.H.,	<i>NIST Standard Reference Database</i>	17,		(1993).	<i>NIST Chemical Kinetics Database - Ver. 5.0,</i>
Melius, C.F.,	<i>in Chemistry and Physics of Energetic Materials, Kluwer Academic Publishers, Dordrecht, 1990</i>				<i>Thermochimistry of Hydrocarbon Intermediates in Combustion: Application of the BAC-MP4 Method,</i>
Miller, J.A. and Bowman, C.T.,	<i>Prog. Energy Comb. Sci.</i>	15,	287	(1989).	<i>Mechanism and modeling of nitrogen chemistry in combustion,</i>
Miller, J.A., Kee, R.J., and Westbrook, C.K.,	<i>Ann. Rev. Phys. Chem.</i>	41,	345-387	(1990).	<i>Chemical kinetics and combustion modeling,</i>
Norton, T.S. and Dryer, F.L.,	<i>Combust. Sci. Technol.</i>	63,	107-129	(1989).	<i>Some new observations on methanol oxidation chemistry,</i>
Norton, T.S.,	<i>Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 1990</i>				<i>The Combustion Chemistry of Simple Alcohol Fuels,</i>
Pedley, J.B., Naylor, R.D., and Kirby, S.P.,	<i>Thermochemical Data of Organic Compounds, Chapman and Hall, NY, 1986.</i>				
Ranzi, E., Sogato, A., Gaffuri, P., Pennati, G., and Faravelli, T.,	<i>Unimolecular Reactions, Wiley Interscience, New York, NY, 1972.</i>				
Robinson, P.J. and Holbrook, K.A.,	<i>J. Chem. Phys.</i>	96,	279-325	(1994).	<i>A wide range modeling study of methane oxidation,</i>
Skinner, G.B., Lifshitz, A., Scheller, K., and Burcat, A.,	<i>NIST Standard Reference Database</i>	56,	3853	(1972).	<i>Kinetics of Methane Oxidation,</i>
Stein, S.E., Rukkers, J.M., and Brown, R.L.,	<i>NSRDS-NBS</i>	25,		(1991).	<i>NIST Structures and Properties Database and Estimation Program,</i>
Stull, D.R. and Prophet, H.,	<i>JANAF Thermochemical Tables,</i>	37,		(1971).	
Stull, D.R., Westrum, E.F., Jr., and Sinke, G.C.,	<i>The Chemical Thermodynamics of Organic Compounds, John Wiley, NY, 1969.</i>				
Tsang, W. and Hampson, R.F.,	<i>J. Phys. Chem. Ref. Data</i>	15,	1087	(1986).	<i>Chemical kinetic data base for combustion chemistry. Part I. Methane and related compounds,</i>

## 6.2. General Thermochemistry and Kinetics

Authors	Journal	Issue	Pages	Year	Title
Warnatz, J.,	<i>in Combustion Chemistry</i> (ed. W.C. Gardiner, Jr.), Springer-Verlag, New York, NY, 1984, p. 197.				
Westbrook, C.K. and Dryer, F.L.,	<i>Combust. Sci. Technol.</i>	20,	125	(1979).	<i>Rate coefficients in the C/H/O system,</i>
Westbrook, C.K. and Dryer, F.L.,	<i>Prog. Energy Combust. Sci.</i>	10,	1-57	(1984).	<i>A comprehensive mechanism for methanol oxidation,</i>
Yetter, R.A., Dryer, F.L., and Rabitz, H.	<i>Combust. Sci. Technol.</i>	79,	97-128	(1991).	<i>Chemical kinetic modelling of hydrocarbon combustion,</i> <i>A comprehensive reaction mechanism for carbon monoxide/hydrogen/oxygen kinetics,</i>



### 6.3. Hydrocarbon Chemistry

Authors	Journal	Issue	Pages	Year	Title
Atri, G.M., Baldwin, R.R., Jackson, D., and Walker, R.W.,	<i>Combust. Flame</i>	30,		1 (1977).	<i>The reaction of OH radicals and HO<sub>2</sub> radicals with carbon monoxide,</i>
Baulch, D.L., Craven, R.J.B., Din, M., Drysdale, D.D., Grant, S., Richardson, D.J., Walker, A., and Watling, G.,	<i>J. Chem. Soc. Faraday Trans. I</i>	79,	689-698	(1983).	<i>Rates of hydroxy radical reactions with methane, ethane, and propane over the temperature range 403-695 K,</i>
Berman, M.R., Fleming, J.W., Harvey, A.B., and Lin, M.C.,	<i>Chem. Phys.</i>	73,	27-33	(1982).	<i>Temperature dependence of the reactions of CH radicals with unsaturated hydrocarbons,</i>
Bowman, C.T.,	<i>Symp. Int. Combust.</i>	15,	869	(1975).	<i>Non-equilibrium radical concentrations in shock-initiated methane oxidation,</i>
Bozzelli, J.W. and Dean, A.M.,	<i>J. Phys. Chem.</i>	94,	3313-3317	(1990).	<i>Chemical activation analysis of the reaction of C2H<sub>5</sub> with O<sub>2</sub>,</i>
Brabbs, T.A., Belles, F.E., and Brokaw, R.S.,	<i>Symp. Int. Combust.</i>	13,	129	(1971).	<i>Shock-Tube Measurements of Specific Reaction Rates in the Branched-Chain H<sub>2</sub>-CO-O<sub>2</sub> System,</i>
Bradley, J. N., Capey, W. D., Fair, R. W. and Pritchard, D. K.,	<i>Inter. J. Chem. Kin.</i>	8,	549-561	(1976).	<i>A shock-tube study of the kinetics of reaction of hydroxyl radicals with H<sub>2</sub>, CO, CH<sub>4</sub>, CF<sub>3</sub>H, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>,</i>
Butler, J.E., Fleming, J.W., Goss, L.P., and Lin, M.C.,	<i>ACS Symp. Ser.</i>	134,	397	(1980).	<i>Kinetics of CH radical reactions important to hydrocarbon combustion systems,</i>
Clark, T.C. and Dove, J.E.,	<i>Can. J. Chem.</i>	51,	2147	(1973).	<i>Examination of possible non-arrhenius behavior in the reactions H + C<sub>2</sub>H<sub>6</sub> H<sub>2</sub> + C<sub>2</sub>H<sub>5</sub>, H + CH<sub>4</sub> H<sub>2</sub> + CH<sub>3</sub>, and CH<sub>3</sub> + C<sub>2</sub>H<sub>6</sub> CH<sub>4</sub> + C<sub>2</sub>H<sub>5</sub>,</i>
Cvetanovic, R.J.,	<i>J. Phys. Chem. Ref. Data</i>	16,	261-302	(1987).	<i>Evaluated chemical kinetic data for the reactions of atomic oxygen O(3P) with unsaturated hydrocarbons,</i>
Dean, A.M., Johnson, R.L., and Steiner, D.C.,	<i>Combust. Flame</i>	37,	41	(1980).	<i>Shock-tube studies of formaldehyde oxidation,</i>
Howard, M.J. and Smith, I.W.M.,	<i>J. Chem. Soc. Faraday Trans. 2</i>	77,	997-1008	(1981).	<i>Direct rate measurements on the reactions N + OH NO + H and O + OH O<sub>2</sub> + H from 250 to 515 K,</i>
Jachimowski, C.J. and Houghton, W.M.,	<i>Combust. Flame</i>	17,	25	(1971).	<i>Shock-tube study of the initiation process in the hydrogen-oxygen reaction,</i>
Kiefer, J.H., Kapsalis, S.A., Al-Alami, M.Z., and Budach, K.A.,	<i>Combust. Flame</i>	51,	79	(1983).	<i>The very high temperature pyrolysis of ethylene and the subsequent reactions of product acetylene,</i>
Klemm, R.B., Skolnik, E.G., Michael, J.V.,	<i>J. Chem. Phys.</i>	72,	1256	(1980).	<i>Absolute rate parameters for the reaction of O(3P) with H<sub>2</sub>CO over the temperature range 250 to 750K,</i>
Messing, I., Filseth, S.V., Sadowski, C.M., and Carrington, T.,	<i>J. Chem. Phys.</i>	74,	3874	(1981).	<i>Absolute rate constants for the reactions of CH with O and N atoms, from 298 to 500K,</i>
Michael, J.V., Nava, D.F., Payne, W.A., and Stief, L.J.,	<i>J. Chem. Phys.</i>	70,	5222	(1979).	<i>Absolute rate constants for the reaction of atomic hydrogen with ketene C<sub>3</sub>H<sub>8</sub> at 295K,</i>
Overend, R. and Paraskevopoulos, G.,	<i>J. Phys. Chem.</i>	82,	1329	(1978).	<i>Rates of OH radical reactions. I. Reactions with H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> at 295K,</i>
Overend, R., Paraskevopoulos, G., and Cvetanovic, R.J.,	<i>Can. J. Chem.</i>	53,	3374	(1975).	<i>Rates of OH radical reaction. I. Reactions with H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> at 295K,</i>

### 6.3. Hydrocarbon Chemistry

Authors	Journal	Issue	Pages	Year	Title
Pagsberg, P., Munk, J., Sillesen, A., and Anastasi,	<i>Cheni. Phys. Lett.</i>	146,	375-381	(1988).	<i>UV spectrum and kinetics of hydroxymethyl radicals,</i>
Paraskevopoulos, G. and Nip, W.S.,	<i>Can. J. Chem.</i>	58,	2146	(1980).	<i>Rates of OH radical reactions. VII. Reactions of OH and OD radicals with n-C4H10, n-CD10, H2 and D2, and of OH with neo-C5H12 at 297K.</i>
Payne, W.A. and Stief, L.J.,	<i>J. Chem. Phys.</i>	64,	1150	(1976).	<i>Absolute rate constant for the reaction of atomic hydrogen with acetylene over an extended pressure and temperature range,</i>
Peeters, J. and Mahnen, G.,	<i>Symp. Int. Combust.</i>	14,	133	(1973).	<i>Reaction mechanisms and rate constants of elementary steps in methane-oxygen flames,</i>
Peeters, J. and Mahnen, G.,	<i>Combust. Inst. European Symp., Academic Press, London, I,</i>	1,	53	(1973).	<i>Structure of Ethylene-Oxygen Flames. Reaction Mechanism and Rate Constants of Elementary Reactions,</i>
Saunders, D. and Heicklen, J.,	<i>J. Phys. Chem.</i>	70,	1950-1958	(1966).	<i>Some reactions of oxygen atoms. I. C2F4, C3F6, C2H2, C2H4, C3H6, 1-C4H8, C2H6, c-C3H6, C3H8,</i>
Sharp, T.E. and Johnston, H.S.	<i>J. Chem. Phys.</i>	37,	1541	(1962).	<i>Hydrogen-deuterium kinetic isotope effect, an experimental and theoretical study over a wide range of temperature,</i>
Stewart, P.H., Smith, G.P., and Golden, D.M.,	<i>Inter. J. Chem. Kin.</i>	21,	923-945	(1989).	<i>The pressure and temperature dependence of methane decomposition,</i>
Sutherland, J.W., Michael, J.V., and Kleemann, R.B., <i>J. Phys. Chem.</i>		90,	5941-5945	(1986).	<i>Rate constant for the O(3P) + CH4 = OH + CH3 reaction obtained by the flash photolysis-shock tube technique over the temperature range 763 &lt; T &lt; 1755 K.</i>
Temps, F. and Wagner, H.Gg.,	<i>Ber. Bunsenges. Phys. Chem.</i>	88,	410-414	(1984).	<i>Kinetics of the reactions of HCO with HCO and O2,</i>
Tully, F.P., Ravishankara, A.R., and Carr, K.,	<i>Inter. J. Chem. Kin.</i>	15,	1111-1118	(1983).	<i>Kinetics of the reactions of the hydroxyl radical with ethane and propane,</i>
Veyret, B. and Lesclaus, R.,	<i>J. Phys. Chem.</i>	85,	1918-1922	(1981).	<i>Absolute rate constants for the reactions of HCO with O2 and NO from 298 to 503 K,</i>
Wagner, A.F. and Wardlaw, D.M.,	<i>J. Phys. Chem.</i>	92,	2462-2471	(1988).	<i>Study of the recombination reaction CH3 + CH3 = C2H6. 2. Theory,</i>
Washida, N., Hatakeyama, S., Takagi, H., Kyogoku, T., and Saito, S.,	<i>J. Chem. Phys.</i>	78,	4533	(1983).	<i>Reaction of ketenes with atomic oxygen,</i>
Westmoreland, P.R.,	<i>Combust. Sci. Technol.</i>	82,	151-168	(1992).	<i>Thermochemistry and kinetics of C2H3 + O2 reactions,</i>
Zabarnick, S., Fleming, J.W., and Lin, M.C.,	<i>Inter. J. Chem. Kin.</i>	20,	117-129	(1988).	<i>Kinetics of hydroxy radical reactions with formaldehyde and 1,3,5-trioxane between 250 and 600 K,</i>

## 6.4. Fluorine Chemistry

Authors	Journal	Issue	Pages	Year	Title
Amos, R.D., Murray, C.W., and Handy, N.C.,	<i>Chem. Phys. Lett.</i>	202,	489-494	(1993).	Structures and vibrational frequencies of <i>FOOF</i> and <i>FONO</i> using density functional theory,
Andersson, K. and Roos, B.O.,	<i>Inter. J. Quant. Chem.</i>	45,	591-607	(1993).	Multiconfigurational second-order perturbation theory: a test of geometries and binding energies,
Appelman, E.H. and Clyne, M.A.A.,	<i>ACS Symp. Ser.</i>	66,	34783	(1978).	Elementary reaction kinetics of fluorine atoms, <i>FO</i> , and <i>NF</i> free radicals,
Bartels, M. and Hoyermann, K.,	<i>An. Asoc. Quim. Argent.</i>	73,	253	(1985).	The rate and the mechanism of the reaction of acetaldehyde with fluorine atoms,
Blauer et al.,				(1971).	
Blauer, J.A.,	<i>J. Phys. Chem.</i>	72,	79	(1968).	The kinetics of dissociation of hydrogen fluoride behind incident shock waves,
Bogar, D.J. and Setser, D.W.,	<i>J. Chem. Phys.</i>	64,	586-602	(1976).	HF infrared chemiluminescence: energy disposal and the role of the radical fragment in the abstraction of hydrogen from polyatomic molecules by F atoms,
Campbell, G.M.,	<i>J. Fluorine Chem.</i>	46,	357-366	(1990).	A kinetic study of the equilibrium between dioxygen monofluoride and dioxygen difluoride,
Clyne, M.A.A. and Hodgson, A.,	<i>Chem. Phys.</i>	79,	351-360	(1983).	Kinetics and detection of <i>F(2P)</i> atoms in a discharge flow system,
Clyne, M.A.A. and Hodgson, A.,	<i>J. Chem. Soc. Faraday Trans. 2</i>	81,	443-455	(1985).	Absolute rate constants for the reaction of fluorine atoms with <i>H<sub>2</sub></i> , <i>CH<sub>2</sub>Cl<sub>2</sub></i> , <i>CH<sub>2</sub>ClF</i> , <i>CH<sub>2</sub>F<sub>2</sub></i> and <i>CHCl<sub>2</sub></i> ,
Czarnowski, J. and Schumacher, H.J.,	<i>Chem. Phys. Lett.</i>	17,	235	(1972).	The kinetics of the thermal decomposition of <i>FO</i> ,
Fettis, G.C., Knox, J.H., and Trotman-Dickenson, A.F.,	<i>J. Chem. Soc., J. Chem. Phys.</i>		1064-1071	(1960).	The reactions of fluorine atoms with alkanes,
Francisco, J.S.,	<i>J. Chem. Phys.</i>	98,	2198-2207	(1993).	An <i>ab initio</i> investigation of the significance of the <i>HOOF</i> intermediate in coupling reactions involving <i>FOOx</i> and <i>HOx</i> species,
Frisch, M.J., Liu, B., Binkley, J.S., Schaefer, H.F., III and Miller, W.H.,	<i>Chem. Phys. Lett.</i>	114,	1	(1985).	Further theoretical examination of the <i>F + H<sub>2</sub></i> entrance channel barrier,
Goldberg, I.B. and Schneider, G.R.,	<i>J. Chem. Phys.</i>	65,	147-153	(1976).	Kinetic study of the reaction of <i>F</i> with <i>H<sub>2</sub></i> and <i>CF<sub>3</sub>H</i> by ESR methods,
Homann, K.H., Schweinfurth, H., and Warmatz, J.,	<i>Ber. Bunsenges. Phys. Chem.</i>	81,	724-728	(1977).	Rate measurements for the reaction of <i>H</i> -atoms with <i>F<sub>2</sub></i> ,
Ioffe, M.A., Gershenson, Yu.M., and Rozenshtein, V.B., Umanskii, S.Ya.,	<i>Chem. Phys. Lett.</i>	154,	131-134	(1989).	Non-Arrhenius behavior of the <i>F+H<sub>2</sub></i> reaction rate at 293-700 K,
Jacobs, T.A., Giedt, R.R., and Cohen, N.,	<i>J. Chem. Phys.</i>	43,	3688	(1965).	Kinetics of decomposition of <i>HF</i> in shock waves,
Johnson, G.K., Smith, P.N., Hubbard, W.N.,	<i>J. Chem. Thermo.</i>	5,	793-809	(1973).	The enthalpies of solution and neutralization of <i>HF(l)</i> , enthalpies of dilution and derived thermodynamic properties of <i>HF(aq)</i> ,
Krech, R.H., Diebold, G.J., and McFadden, D.L.,	<i>J. Am. Chem. Soc.</i>	99,	4605	(1977).	Kinetics of the <i>O + F<sub>2</sub></i> reaction. A case of low reactivity of elemental fluorine,
Manning, R.G., Grant, E.R., Merrill, J.C., Parks, N.J., and Root, J.W.,	<i>Inter. J. Chem. Kin.</i>	7,	39-44	(1975).	Hydrogen abstraction by fluorine atoms under conditions of thermal initiation: Hydrocarbons and fluorinated hydrocarbons,

## 6.4. Fluorine Chemistry

Authors	Journal	Issue	Pages	Year	Title
Manocha, A.S., Setser, D.W., and Wickramaaratchi, M.A., Pollock, T.I. and Jones, W.E., Rowland, F.S., Rust, F., and Frank, J.P., Seeger, C., Roitzoll, G., Lubbert, A., and Schugert, K., Stevens, P.S., Brune, W.H., and Anderson, J.G., Tang, Y.-N., Smail, T., and Rowland, F.S., Wagner, H.G., Warmatz, J., and Zetzsch, C., Wallington, T.J. and Hurley, M.D., Wallington, T.J., Hurley, M.D., Shi, J.C., Maricq, M.M., Sehested, J., Nielsen, O.J., and Ellermann, T., Walther, C.D. and Wagner, H.G., Williams, R.L. and Rowland, F.S., Wurzberg, E. and Houston, P.L., Zelenov, V.V., Kukui, A.S., Dodonov, A.F., Aleinikov, N.N., Kashtanov, S.A., and Turchin, A.V., Zhao, Y. and Francisco, J.S.,	<i>J. Chem. Phys.</i> <i>Can. J. Chem.</i> <i>ACS Symp. Ser.</i> <i>Inter. J. Chem. Kin.</i> <i>J. Phys. Chem.</i> <i>J. Am. Chem. Soc.</i> <i>An. Asoc. Quim. Argent.</i> <i>Inter. J. Chem. Kin.</i> <i>Ber. Bunsenges. Phys. Chem.</i> <i>J. Phys. Chem.</i> <i>J. Chem. Phys.</i> <i>Khim. Fiz.</i> <i>Chem. Phys. Lett.</i>	76, 51, 66, 13, 93, 91, 59, 25, 25, 87, 77, 72, 10, 167,	129?? 2041-2046 26-58 39-58 4068-4079 2120-2131 169 819-824 651-665 403-409 301-307 5915 1121-1124 285-290	(1983). of groups III, IV, and V; (1973). Gas phase reactions of fluorine atoms, Reaction of radioactive ( <sup>18</sup> F) with alkynes, alkynes, and other substrates, (1981). Kinetic and mechanistic investigations of F + H <sub>2</sub> O/D <sub>2</sub> O and F + H <sub>2</sub> D <sub>2</sub> over the temperature range 240-373 K, Reactions of energetic fluorine-18 atoms with fluoromethanes. Formation of CH <sub>18</sub> F and CF <sub>18</sub> F, On the reaction of F atoms with methone, A kinetic study of the reaction of chlorine and fluorine atoms with CF <sub>3</sub> CHO at 295 +/- 2K, A kinetic study of the reaction of fluorine atoms with CH <sub>3</sub> F, CH <sub>3</sub> Cl, CH <sub>3</sub> Br, CF <sub>2</sub> H <sub>2</sub> , CO, CF <sub>3</sub> H, CF <sub>3</sub> CHCl <sub>2</sub> , CF <sub>3</sub> CH <sub>2</sub> F, CHF <sub>2</sub> CH <sub>2</sub> , CF <sub>2</sub> ClCH <sub>3</sub> , CHF <sub>2</sub> CH <sub>3</sub> , and CF <sub>3</sub> CF <sub>2</sub> H at 295 +/- 2K, Über die reaktionen von F-atomen mit H <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub> und NH <sub>3</sub> , Hydrogen atom abstraction by fluorine atoms, The temperature dependence of hydrogen abstraction reactions: F+HCl, F+HBr, F+DBr, and F+I, Mass-spectrometric determination of constants of reaction rate of atoms-H with molecules-F <sub>2</sub> , xenon and krypton fluorides in 298-505-K temperature range. 2. Reaction of H+ KrF <sub>2</sub> , <i>Ab initio</i> studies of the structure and thermochemistry of FOr radicals,	(1983). 1973). 1978). 1981). 1989). 1969). 1971). 1999). 1993). (1983). 1973). 1980). (1991). (1990).

## 6.5. Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Allen, T.L.,	<i>J. Chem. Phys.</i>	31,	1039-1049	(1959).	<i>Bond energies and the interactions between next-nearest neighbors. I. Saturated hydrocarbons, diamond, sulfanes, S8, and organic sulfur compounds,</i>
Amphlett, J.C. and Whittle, E.,	<i>Trans. Faraday Soc.</i>	64,	2130-2142	(1968).	<i>Bromination of fluoralkanes. Part 4. Kinetics of thermal bromination of fluoroform and pentfluoroethane,</i>
Arthur, N.L. and Gray, P.,	<i>Trans. Faraday Soc.</i>	65,	434-440	(1969).	<i>Isotope effects in reactions of trifluoromethyl radicals with hydrogen chloride and hydrogen sulphide,</i>
Bassett, J.E. and Whittle, E.,	<i>J. Chem. Soc. Faraday Trans. 1</i>	68,	492-498	(1972).	<i>Reaction of C2F5 radicals with HCl. Determination of the bond dissociation energy D(C2F5-H),</i>
Berman, D.W., Bomse, D.S., and Beauchamp, J.L.,	<i>Int. J. Mass Spectrom. Ion Phys.</i>	39,	26	(1981).	
Bernstein, H.J.,	<i>J. Phys. Chem.</i>	69,	1550-1564	(1965).	<i>Bond and interaction contributions for calculating the heat of formation, diamagnetic susceptibility, molar refraction and volume, and thermodynamic properties of some substituted methanes,</i>
Bibby, M.M. and Carter, G.,	<i>Trans. Faraday Soc.</i>	62,	2637	(1966).	<i>C-F bond dissociation energies in perfluorocarbon gases using negative ion appearance potential data,</i>
Bryant, W.M.D.,	<i>J. Polymer Sci.</i>	56,	277-296	(1962).	<i>Thermodynamics of formation and depolymerization of polytetrafluoroethylene,</i>
Buckley, G.S. and Rodgers, A.S.	<i>J. Phys. Chem.</i>	86,	2059-2062	(1982).	<i>Electrostatic model for the heats of formation and dipole moments of chlorine- and fluorine-substituted methanes,</i>
Burgess, D.R.F. Jr., Westmoreland, P.R., Tsang, W., and Zachariah, M.R.,	<i>in Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays (eds. W.L. Grosshandler, R.G. Gann, and W.M. Pitts), NIST Special Publication 861, 1994, pp. 467-507</i>				
Burgess, D.R.F. Jr., Zachariah, M.R., Tsang, W., and Westmoreland, P.R., Carlson, G.A., Chang, H.W., Craig, N.L., and Setser, D.W., Chao, J., Rodgers, A.S., Wilhoit, R.C., and Zwolinski, B.J., Chen, S.S., Rodgers, A.S., Chao, J., Wilhoit, R.C., and Zwolinski, B.J., Chen, S.S., Wilhoit, R.C., and Zwolinski, B.J., Chen, Y., Rauk, A., and Tschukow-Roux, E.,	<i>ACS Symp. Ser.</i>	in press	(1995).		<i>Kinetics of fluorine-inhibited flames, Key species and important reactions in fluorinated hydrocarbon flame chemistry, A shock tube study of the C2F4-CF2 equilibrium, Nonequilibrium unimolecular reactions and collisional deactivation of chemically-activated fluoroethane and 1,1,1-trifluoroethane, Ideal gas thermodynamic properties of six chloroethanes, Ideal gas thermodynamic properties of six chlorofluoromethanes, Structures, barriers for internal rotation, vibrational frequencies, and thermodynamic function of CH2FCH2, CHF2CH2, and CF3CH2 radicals: an ab initio study,</i>

## 6.5. Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Chen, Y., Rauk, A., and Tschuikow-Roux, E.,	<i>J. Chem. Phys.</i>	93,	1187-1195	(1990).	<i>Structures, barriers for rotation and inversion, vibrational frequencies, and thermodynamic function of ethyl, 1-fluoroethyl, and 1,1-difluoroethyl radicals: an ab initio study,</i>
Chen, Y., Rauk, A., and Tschuikow-Roux, E.,	<i>J. Chem. Phys.</i>	95,	2774-2786	(1991).	<i>Structures, barriers for internal rotation and inversion, vibrational frequencies, and thermodynamic functions of CH<sub>2</sub>FCF<sub>2</sub>, CHF<sub>2</sub>CF<sub>2</sub>, and CF<sub>3</sub>CF<sub>2</sub> radicals: an ab initio study,</i>
Chen, Y., Rauk, A., and Tschuikow-Roux, E.,	<i>J. Chem. Phys.</i>	94,	7299-7310	(1991).	<i>Structures, barriers for internal rotation, vibrational frequencies, and thermodynamic functions of CH<sub>2</sub>CHF, CHF<sub>2</sub>CHF, and CF<sub>3</sub>CHF radicals: an ab initio study,</i>
Coomber, J.W. and Whittle, E.,	<i>Trans. Faraday Soc.</i>	62,	2183-2190	(1966).	<i>Photochlorination of methane and fluoroform. Dissociation energy D(CF<sub>3</sub>-H) and entropy of CF<sub>3</sub> radical,</i>
Coomber, J.W. and Whittle, E.,	<i>Trans. Faraday Soc.</i>	63,	608-619	(1967).	<i>Bond dissociation energies from equilibrium studies. Part I. D(CF<sub>3</sub>-CF<sub>3</sub>) and enthalpy of formation of C<sub>2</sub>F<sub>6</sub>,</i>
Coomber, J.W. and Whittle, E.,	<i>Trans. Faraday Soc.</i>	63,	1394-1401	(1967).	<i>Bond dissociation energies from equilibrium studies. Part 2. D(CF<sub>3</sub>-CF<sub>3</sub>) and enthalpy of formation of C<sub>2</sub>F<sub>6</sub>,</i>
Coomber, J.W. and Whittle, E.,	<i>Trans. Faraday Soc.</i>	63,	2656-2667	(1967).	<i>Bond dissociation energies from equilibrium studies. Part 3. D(CF<sub>3</sub>-CH<sub>3</sub>) D(C<sub>2</sub>F<sub>5</sub>-Cl), and the enthalpy of formation of CF<sub>3</sub>Cl molecules,</i>
Cooper, D.L., Allan, N.L., and Powell, R.L.,	<i>J. Fluorine Chem.</i>	46,	317-337	(1990).	<i>Theoretical studies of fluorocarbons. Part I. Small perfluoralkane molecules,</i>
Cooper, D.L., Allan, N.L., and Powell, R.L.,	<i>J. Fluorine Chem.</i>	49,	421-432	(1990).	<i>Theoretical studies of fluorocarbons. Part III. Primary, secondary, tertiary and quaternary centres,</i>
Cooper, D.L., Wright, S.C., Allan, N.L., and Winterton, N.,	<i>J. Fluorine Chem.</i>	47,	489-507	(1990).	<i>Theoretical studies of fluorocarbons. Part II. Fluorine and chlorine substituted alkanes,</i>
Corbett, P., Tarr, A.M and Whittle, E.,	<i>Trans. Faraday Soc.</i>	59,	1609-1618	(1963).	<i>Vapour-phase bromination of fluoroform and methane,</i>
Cox, J.D. and Pilcher, G.,	<i>Thermochemistry of Organic and Organometallic Compounds</i>				<i>Academic Press, New York, NY, 1970.</i>
Cox, J.D., Gundry, H.A., and Head, A.J.,	<i>J. Trans. Faraday Soc.</i>	61,	1594	(1965).	<i>Thermodynamic properties of fluorine compounds,</i>
Daubert, T.E. and Danner, R.P.,	<i>NIST Standard Reference Database</i>	11,		(1985).	<i>DIPPR Data Compilation of Pure Compound Properties,</i>
Dibeler, V.H. and Reese, R.M.,	<i>J. Res. NBS</i>	54,	127	(1955).	<i>Selected positive and negative ions in the mass spectra of the monohalomethanes,</i>
Dixon, D.A., Matsuzawa, N., and Walker, S.C.,	<i>J. Phys. Chem.</i>	96,	0740-10746	(1992).	<i>Conformational analysis of 1,2-dihaloethanes - A comparison of theoretical methods,</i>
Domalski, E.S. and Armstrong, G.T.,	<i>J. Res. NBS A</i>	71,	105	(1967).	
Duus, H.C.,	<i>Ind. Eng. Chem.</i>	47,	1445-1449	(1955).	
Edwards, J.W. and Small, P.A.,	<i>Ber. Bunsenges. Phys. Chem.</i>	202,	71329	(1964).	<i>Pyrolysis of chlorodifluoromethane and difluoromethylene,</i>
Ehlert, T.C.,	<i>J. Phys. Chem.</i>	73,	949	(1969).	<i>Bonding in C1 and C2 fluorides,</i>
Farber, M., Frisch, M.A., and Ko, H.C.,	<i>Trans. Faraday Soc.</i>	65,	3202-3209	(1969).	<i>Thermodynamic properties of CF and CF<sub>2</sub> from molecular effusion, and mass spectrometry investigations,</i>

## 6.5. Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Ferguson, K. C and Whittle, E.,	<i>J. Chem. Soc. Faraday Trans.</i>	68,	306	(1972).	<i>Kinetics of the reaction between HBr and C2F5Br,</i>
Ferguson, K. C and Whittle, E.,	<i>J. Chem. Soc. Faraday Trans. I</i>	68,	641-646	(1972).	<i>Competitive study of the reactions Br + RBr = Br2 + R (R = CF3, C2F5)</i>
Ferguson, K. C and Whittle, E.,	<i>J. Chem. Soc. Faraday Trans. I</i>	68,	295-305	(1972).	<i>Kinetics of the reaction between HBr and CF3Br. Determination of the bond dissociation energy D(CF3-Br),</i>
Fisher, I.P., Homer, J.B., and Lossing, F.P.,	<i>J. Am. Chem. Soc.</i>	87,	957	(1965).	<i>Free radicals by mass spectrometry. XXXIII. Ionization potentials of CF2, CF3CF2, CF3CH2, n-C3F7, and I-C3F7 radicals,</i>
Francisco, J.A., Ghoul, W.A., and Williams, I.H.,	<i>Theorchem. - J. Mol. Struct.</i>	98,	35-39	(1993).	<i>Thermochemistry of possible degradation pathways for compounds CF3CHXY(X, Y = H, F, Cl) using AM1 and MNDO semiempirical methods,</i>
Francisco, J.S., Ghoul, W.A., and Williams, I.H.,	<i>J. Mol. Struct. (Theochem)</i>	279,	35-39	(1993).	<i>Thermochemistry of possible degradation pathways for compounds CF3CHXY (X, Y=H,F,Cl) using AM1 and MNDO semiempirical methods,</i>
Friesen, D., Hedberg, K.,	<i>J. Am. Chem. Soc.</i>	102	3987-3994	(1980).	<i>Conformational analysis. 7. 1,2-difluoroethane. An electron-diffraction investigation of the molecular structure, composition, trans-gauche energy and entropy differences and potential hindering internal rotation.,</i>
Funk, E.W. and Prausnitz, J.M.,	<i>J. Phys. Chem.</i>	75	2530-2532	(1971).	<i>Europes of vaporization for fluorocarbons and hydrocarbons from the Hildebrand Rule,</i>
Gelles, E. and Pitzer, K.S.,	<i>J. Am. Chem. Soc.</i>	75,	5259-5267	(1953).	<i>Thermodynamic functions of halogenated methanes,</i>
Golden, D.M. and Benson, S.W.,	<i>Chem. Rev.</i>	69,	125	(1969).	
Good, W.D., Scott, D.W., and Waddington, G.,	<i>J. Phys. Chem.</i>	60,	1080-1089	(1956).	<i>Combustion calorimetry of organic fluorine containing compounds by a rotating bomb method.</i>
Goy, C.A., Lord, A., and Pritchard, H.O.,	<i>J. Phys. Chem.</i>	71,	1086-1088	(1967).	<i>Kinetics and thermodynamics of the reaction between iodine and fluoroforn and the heat of formation of trifluoromethyl iodide,</i>
Greenberg, E. and Hubbard,	<i>J. Phys. Chem.</i>	72,	222-227	(1968).	<i>Fluorine bomb calorimetry. XXIII. The enthalpy of formation of carbon tetrafluoride.</i>
Gurvich, L.V., Veyts, I.V., and Alcock, C.B.	<i>Thermodynamic Properties of Individual Substances, Hemisphere Pub. Corp., New York, NY, 1991.</i>				
Heras, J.M., Arvia, A.J., Aymonino, P.J., and Schumacher, H.J.,	<i>An. Assoc. Quim. Argent.</i>	50,	120	(1962).	<i>Estudio cinetico de la reaccion termica entre fluor, monoxido de carbono y oxigeno,</i>
Hildenbrand, D.L.,	<i>Chem. Phys. Lett.</i>	32,	523-526	(1975).	<i>Dissociation energy and ionization potential of the molecule CF</i>
Iwaoka, T., Kaneko, C., Shighara, A., and Ichikawa, H.,	<i>J. Phys. Org. Chem.</i>	6,	195-200	(1993).	<i>Mechanism of syn addition of molecular fluorine to ethylene - An ab initio MO study,</i>
Kerr, J.A. and Timlin, D.M.,	<i>Inter. J. Chem. Kin.</i>	3,	427-441	(1971).	<i>A kinetic study of the thermal elimination of hydrogen fluoride from 1,2-difluoroethane. Determination of the bond dissociation energies D(CH2F-CH2F) and D(CH2F-H),</i>
Kirkbride, F.W. and Davidson, F.G.,	<i>Nature</i>	174,	79-80	(1954).	
Kolesov, T.S. and Papina, T.S.,	<i>Russ. J. Phys. Chem.</i>	44,	611	(1970).	

## 6.5. Fluorocarbon Thermochimistry

Authors	Journal	Issue	Pages	Year	Title
Kolesov, V.P. and Papina, T.S.,	Russ. Chem. Rev.	52,	425-439	(1983).	<i>Thermochimistry of haloethanes,</i>
Kolesov, V.P.,	Russ. Chem. Rev.	47,	1145-1168	(1978).	<i>Thermochimistry of halogenomethanes,</i>
Kolesov, V.P., Martynov, A.M., Shtekher, S.M., and Skuratov, S.M.,	Zhur. Fiz. Khim.	36,	2078	(1962).	
Kolesov, V.P., Martynov, A.M., and Skuratov,	Russ. J. Phys. Chem.	39	223	(1965).	
Kolesov, V.P., Shtekher, S.N., Martynov, A.M., and Skuratov, S.M.,	Russ. J. Phys. Chem.	42,	975	(1968).	
Kolesov, V.P., Zenkov, I.D., and Skuratov, S.M.	Zh. Fiz. Khim.	36,	89-92	(1962).	
Kotaka, M., Sato, S., and Shimokoshi, K.,	J. Fluorine Chem.	41,	371-382	(1988).	<i>INDO study of 1,2-fluorine atom migration in 1,1,2,2-tetrafluoroethyl radical, cation, and anion,</i>
Kudchadker, S.A. and Kudchadker, A.P.,	J. Phys. Chem. Ref. Data	7,	1285-1307	(1978).	<i>Ideal gas thermodynamic properties of CH<sub>4-(a+b+c+d)FaClBrCl</sub></i>
Kudchadker, S.A. and Kudchadker, A.P.,	J. Phys. Chem. Ref. Data	8,	519-526	(1979).	<i>Ideal gas thermodynamic properties of selected bromoethanes and iodoethane,</i>
Lacher, J.R. and Skinner, H.A.,	J. Chem. Soc. A.	5,	1034-1038	(1968).	<i>Bond energy additivity and bond interactions in fluoro-halogenated hydrocarbons,</i>
Lacher, J.R., Casali, L., and Park, J.D.,	J. Phys. Chem.	60,	608	(1956).	<i>Reaction heats of organic halogen compounds. V. The vapor phase bromination of tetrafluoroethylene and trifluorochloroethylene,</i>
Lacher, J.R., Kianpour, A., Oetting, F., and Park, J.D.,	Trans. Faraday Soc.	52,	1500-1508	(1956).	<i>Reaction calorimetry: The hydrogenation of organic fluorides and chlorides,</i>
Lacher, J.R., Kianpour, A., and Park, J.D.,	J. Phys. Chem.	60,	1454-1455	(1956).	<i>Reaction heats of organic halogen compounds. VI. The catalytic hydrogenation of some alkyl fluorides,</i>
Lacher, J.R., Lea, K.R., Walden, C.H., Olson, G.G., and Park, J.D.,	J. Am. Chem. Soc.	72,	3231	(1950).	
Lacher, J.R., McKinley, J.J., Snow, C.M., Michel, L., Nelson, G., and Park, J.D.,	J. Am. Chem. Soc.	71,	1330-1334	(1949).	
Lias, S.G.,	ACS Symp. Ser.	66,	152-187	(1978).	<i>Ion-molecule reactions involving fluorine-containing organic compounds,</i>
Lias, S.G., Karpas, Z., and Liebman, J.F.,	J. Am. Chem. Soc.	107,	6089-6096	(1985).	<i>Halomethene: effects of halogen substitution on absolute heats of formation,</i>
Lifshitz, A. and Grajower, R.	Inter. J. Mass Spec. Ion Phys.	10,	25	(1972).	<i>Dissociative electron capture and dissociative ionization in perfluorocyclobutane,</i>
Lossing, F.P., Ingold, K.V., and Henderson, I.H.S.,	J. Chem. Phys.	22,	1489-1492	(1954).	<i>Free radicals by mass spectrometry. VI. The bond dissociation energies of some methyl, allyl, and benzyl compounds by electron impact,</i>
Luo, Y.-R. and Benson, S.W.,	J. Phys. Chem.	92,	5255-5257.		<i>New electronegativity scale for the correlation of heats of formation. I. Alkyl derivatives,</i>
MacNeil, K.A.G. and Thyne, J.C.I.	Inter. J. Mass Spec. Ion Phys.	3,	35-46	(1969).	<i>The deconvolution of negative ion data,</i>

## 6.5. Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Martell, J.M. and Boyd, R.J.,	<i>J. Phys. Chem.</i>	96,	6287-6290	(1992).	<i>An ab initio study of the series C2HnFn-n (n=0-6): geometries, total energies, and C-C bond dissociation energies,</i>
Martin, J.-P. and Paraskevopoulos, G.,	<i>Can. J. Chem.</i>	61,	861	(1983).	<i>A kinetics study of the reactions of OH radicals with fluorohanes, Estimates of C-H bond strength in fluoralkanes,</i>
Masri, A.R.,	<i>Symp. Int. Combust.</i>	24,		(1992).	<i>Structure of laminar nonpremixed flames of methane inhibited with CF3Br,</i>
Mastrukov, V.S., Boggs, J.E. and Samdal, S.,	<i>J. Mol. Struct. (Theochem.)</i>	283,	199-206	(1993).	<i>Structural changes as a function of torsional motion studied by ab initio calculations. Part I. X3A-AX3 (A = C, Si, Ge and X = H, F, Cl),</i>
McMillen, D.F. and Golden, D.M.,	<i>Ann. Rev. Phys. Chem.</i>	33,	493	(1982).	<i>Hydrocarbon bond dissociation energies,</i>
Melius, C.F.,	<i>in Chemistry and Physics of Energetic Materials, Kluwer Academic Publishers, Dordrecht, 1990</i>				<i>Thermochimistry of Hydrocarbon Intermediates in Combustion: Application of the BAC-MP4 Method,</i>
Melius, C.F.,					<i>personal communication, January, 1993.</i>
Minato, T., Yamabe, S., Fujimoto, H., and Fukui, K.,	<i>Bull. Chem. Soc. Jpn.</i>	51,	34709	(1978).	<i>A molecular orbital calculation of chemically interacting systems. Interaction between two radicals,</i>
Modica, A.P.,	<i>J. Chem. Phys.</i>	44,	1585	(1966).	
Neugebauer, C.A. and Margrave, J.L.,	<i>J. Phys. Chem.</i>	60,	1318-1321	(1956).	<i>The heats of formation of tetrafluoroethylene, tetrafluoromethane, and 1,1-difluoroethylene,</i>
Neugebauer, C.A. and Margrave, J.L.,	<i>J. Phys. Chem.</i>	62,	1043-1048	(1958).	<i>The heats of formation of CHF3 and CH2F2,</i>
Nyden, M.R.,					<i>personal communication, November, 1993.</i>
Okafo, E.N. and Whittle, E.,	<i>Chem. Soc. Faraday Trans. 1</i>	70,	1366-1375	(1974).	<i>Bond dissociation energies from equilibrium studies. Part 5. The equilibria Br2 + CH2F2 = HBr + CHF2Br and Br2 + CH3F = HBr + CH2FB. Determination of D(CHF2-Br) and Hj(CHF2Br,g),</i>
Okafo, E.N. and Whittle, E.,	<i>Inter. J. Chem. Kin.</i>	7,	287-300	(1975).	<i>Competitive study of the reactions of Br + Rf = IBr + Rf and determination of bond dissociation energies D(Rf-I) where Rf = CF3, C2F5, n-C3F7, i-C3F7, and n-C4F9,</i>
Paulino, J.A. and Squires, R.R.,	<i>J. Am. Chem. Soc.</i>	113	5573-5580	(1991).	<i>Carbene thermochemistry from collision-induced dissociation threshold energy measurements. The heats of formation of XIAl CF2 and XIAl CC12,</i>
Pedley, J.B., Naylor, R.D., and Kirby, S.P.,	<i>Thermochemical Data of Organic Compounds, Chapman and Hall, NY, 1986.</i>				
Pickard, J.M. and Rodgers, A.S.,	<i>Inter. J. Chem. Kin.</i>	15,	569-577	(1983).	<i>Kinetics of the gas phase reaction CH3F + I2 = CH2FI + HI: The C-H bond dissociation energy in methyl and methylene fluorides,</i>
Pickard, J.M. and Rodgers, A.S.,	<i>J. Am. Chem. Soc.</i>	98,	6115-6118	(1976).	<i>Kinetics of the gas phase addition of bromine to 1,1-difluoroethylene. Pi bond dissociation energy of 1,1-difluoroethylene,</i>
Pickard, J.M. and Rodgers, A.S.,	<i>J. Am. Chem. Soc.</i>	99,	695-696	(1977).	<i>Pi bond dissociation energy in 1,1-difluoroethylene,</i>
Pickard, J.M. and Rodgers, A.S.,	<i>J. Am. Chem. Soc.</i>	99,	691-694	(1977).	<i>The kinetics and thermochemistry of the reaction of 1,1-difluoroethane with iodine. The CF2-H bond dissociation energy in 1,1-difluoroethyl, and the heat of formation of 1,1-difluoroethyl,</i>
Pottie, R.F.,	<i>J. Chem. Phys.</i>	42,	2607	(1965).	<i>Ionization potential and the heat of formation of the difluoromethylene radical,</i>

## 6.5. Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Pritchard, G.O. and Perona, M.J.,	<i>Inter. J. Chem. Kin.</i>	1,	509-525	(1969).	Some hydrogen atom abstraction reactions of $CF_2H$ and $CFH_2$ radicals, and the C-H bond dissociation energy in $CF_2H_2$ .
Pritchard, G.O. and Thommason, R.L.,	<i>J. Phys. Chem.</i>	68,	568-571	(1964).	The C-H bond dissociation energies in $CF_3H$ , $C_2F_5H$ , and $C_3F_7H$ .
Pritchard, G.O., Nilsson, W.B., and Kirtman, B.,	<i>Inter. J. Chem. Kin.</i>	16,	1637-1643	(1984).	Orbital energy and entropy correlations for disproportionation versus combination in the reactions of $CF_xH(3-x)$ radicals ( $x=0, 1, 2, 3$ ) with ethyl radicals. The heat of formation of fluoromethylene,
Pritchard, G.O., Pritchard, H.O., and Trotman-Dickenson, A.F.,	<i>Chem. Ind.</i>		564	(1955).	
Rodgers, A.S., Chao, J., Wilhoit, R.C., and Zwolinski, B.J.,	<i>J. Phys. Chem. Ref. Data</i>	3,	117-140	(1974).	Ideal gas thermodynamic properties of eight chloro- and fluoromethanes,
Rodgers, A.S. and Ford, W.G.F.,	<i>Inter. J. Chem. Kin.</i>	5,	965-975	(1973).	Analysis of the kinetics of the thermal and chemically activated elimination of HF from 1,1,1-trifluoroethane. The C-C bond dissociation energy and the heat of formation of 1,1,1-trifluoroethane,
Rodgers, A.S.,	<i>ACS Symp. Ser.</i>	66,	296	(1978).	Thermochimistry of fluorocarbon radicals,
Rodgers, A.S.,	<i>J. Phys. Chem.</i>	71,	1996-2000	(1967).	Estimation of the heats of formation of chlorofluorocarbons,
Rodgers, A.S.,	<i>TRC Thermochemistry Tables, Texas A&amp;M University, College Station TX</i> ,				
Russo, N., Sicilia, E., Toscano, M.,	<i>J. Chem. Phys.</i>	97,	5031-5036	(1992).	Geometries, singlet-triplet separations, dipole moments, ionization potentials, and vibrational frequencies in methylene ( $CH_2$ ) and halocarbenes ( $CHF$ , $CF_2$ , $CCl_2$ , $CB_2$ , and $Cl_2$ ),
Sana, M., Leroy, G., Peeters, D., and Wilante, C.,	<i>Theochem.</i>	41,	249-274	(1988).	The theoretical study of the heats of formation of organic compounds containing the substituents, $CH_3$ , $CF_2$ , $NH_2$ , $NF_2$ , $NO_2$ , $OH$ and $F$ ,
Schnieder, W.F. and Wallington, T.J.,	<i>J. Phys. Chem.</i>	98,	7448	(1994).	
Scott, D.W., Good, W.D., and Waddington, G.,	<i>J. Am. Chem. Soc.</i>	77,	245-246	(1955).	Heat of formation of tetrafluoromethane from combustion calorimetry of polytetrafluoroethylene,
Scott, D.W., Good, W.D., and Waddington, G.,	<i>J. Phys. Chem.</i>	60,	1080	(1956).	
Sinke, G.C.,	<i>J. Phys. Chem.</i>	70,	1326	(1966).	
Skinner, H.A.,	<i>Adv. Organometal. Chem.</i>	2,	49	(1965).	
Sianina, Z.,	<i>Thermochim. Acta</i>	181,	119-125	(1991).	Conformers of 1,2-difluoroethane: their thermodynamic interplay and the extremum temperature course of some terms,
Slayden, S.V., Liebman, J.F., and Mallard, W.G.,	<i>preprint</i>				Thermochimistry of halogenated organic compounds
Somayajulu, G.R. and Zwolinski, B.J.	<i>J. Chem. Soc. Faraday Trans. II</i>	70,	967-972	(1974).	Generalized treatment of alkanes. Part 3. Triatomic additivity,
Somayajulu, G.R. and Zwolinski, B.J.	<i>J. Chem. Soc. Faraday Trans. II</i>				Part 4. Triatomic additivity,
Spyrou, S.M., Sauers, I., and Christophorous, L.G.,	<i>J. Chem. Phys.</i>	70,	973-993	(1974).	Generalized treatment of alkanes. Part 4. Triatomic additivity. applications to substituted alkanes,
Stadelmann, J.P. and Vogt, J.,	<i>Inter. J. Mass Spectrom. Ion Phys.</i>	35,	83	(1980).	Electron attachment to the perfluoroalkanes $n$ -CN $F_2N+2$ ( $N=1-6$ ) and $i$ -C $4F_{10}$ ,

## 6.5. Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Staemmler, V.,	Theoret. Chim. Acta	35,	309-327	(1974).	<i>Ab initio calculation of the lowest singlet and triplet states in CH<sub>2</sub>, CHF, CF<sub>2</sub>, and CHCH<sub>3</sub>,</i>
Stein, S.E., Rukkers, J.M., and Brown, R.L.,	NIST Standard Reference Database	25,		(1991).	<i>NIST Structures and Properties Database and Estimation Program,</i>
Stull, D.R. and Prophet, H.,	NSRDS-NBS	37,		(1971).	<i>JANAF Thermochemical Tables,</i>
Stull, D.R., Westrum, E.F., Jr., and Sinke, G.C.,	<i>The Chemical Thermodynamics of Organic Compounds.</i> John Wiley, NY, 1969.				
Thyneec, J.C.J. and MacNeil, K.A.G.,	Inter. J. Mass Spec. Ion Phys.	5,	329-335	(1970).	<i>Ionisation of tetrafluoroethylene by electron impact,</i>
Tsang, W.,	J. Phys. Chem.	90,	414-418	(1986).	<i>Single pulse shock tube study on the stability of perfluorobromooctane,</i>
Tschukow-Roux, E. and Salomon, D.R.,	J. Phys. Chem.	91,	699-702	(1987).	<i>Photoionization of C<sub>2</sub>H<sub>5</sub>Cl in the presence of C<sub>2</sub>H<sub>6</sub>. The heat of formation of the CH<sub>3</sub>CHCl radical and the Do (CH<sub>3</sub>CHCl-H) bond dissociation energy,</i>
Tschukow-Roux, E.,	J. Phys. Chem.	69,	1075-1077	(1965).	
Tschukow-Roux, E., Salomon, and Paddison, S.,	J. Phys. Chem.	91,	3037-3040	(1987).	<i>Reaction of atomic bromine with ethyl bromide. The heat of formation of the CH<sub>3</sub>CHBr radical and the a-carbon-hydrogen bond dissociation energy,</i>
Tsuda, S., Melton, C.E., and Hamill, W.H.,	J. Chem. Phys.	41,	689	(1964).	<i>Ionization efficiency curves for molecular and fragment ions from methane and the methyl halides,</i>
von Wartenberg, H. and Schiefer, J.,	Z. Anorg. Allg. Chem.	278,	326-332	(1955).	
Walker, L.C., Sinke, G.C., Perettie, D.J., and Janz, G.J.,	J. Am. Chem. Soc.	92,	4525	(1970).	
Walter, T.A., Livishitz, C., Chupka, W.A., and Berkowitz, J.,	J. Chem. Phys.	51,	3531	(1969).	<i>Mass-spectrometric study of the photoionization of C<sub>2</sub>F<sub>4</sub> and CF<sub>4</sub>,</i>
Williamson, A.D., LeBreton, P.R., and Beauchamp, J.L.,	J. Am. Chem. Soc.	98,	2705	(1976),	
Wood, J.L., Lagow, R.J., and Margrave, J.L.,	J. Chem. Eng. Data	12,	255	(1967).	
Wu, E.-C. and Rodgers, A.S.,	J. Phys. Chem.	78,	2315-2317	(1974).	<i>Thermochimistry of gas-phase equilibrium CF<sub>3</sub>CH<sub>3</sub>+I<sub>2</sub>=CF<sub>3</sub>CH<sub>2</sub>I+HI. The carbon-hydrogen bond dissociation energy in 1,1,1-trifluoroethane and the heat of formation of the 2,2,2-trifluoroethyl radical,</i>
Wu, E.C. and Rodgers, A.S.,	J. Am. Chem. Soc.	98,	6112	(1976).	<i>Kinetics of the gas phase reaction of pentfluoroethyl iodide with hydrogen iodide. Enthalpy of formation of the pentfluoroethyl radical and ...</i>
Zachariah, M.R., Tsang, W., Westmoreland, P.R., and Burgess, D.R.F. Jr.,	J. Phys. Chem.			submitted (1995).	<i>Theoretical prediction of the thermochimistry and kinetics of reactions of CF<sub>2</sub>O with hydrogen atoms and water,</i>
Zachariah, M.R., Westmoreland, P.R., Burgess, D.R.F. Jr., Tsang, W., and Melius, C.F.,	ACS Symp. Ser.			in press (1995).	<i>Theoretical prediction of thermochemical and kinetic properties of fluorocarbons,</i>

## 6.5. Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Zachariah, M.R., Westmoreland, P.R., Burgess, D.R.F. Jr., Tsang, W., and Melius, C.F., Zahn, C.T.,	<i>J. Phys. Chem.</i> <i>J. Chem. Phys.</i>		submitted	(1995).	<i>Thermochemical data for C1 and C2 hydrofluorocarbons and oxidized hydrofluorocarbons: BAC-MP4 ab initio predictions for stable and radical species</i>
Zmbov, K.F., Uy, O.M., and Margrave, J.L.,	<i>J. Am. Chem. Soc.</i>	2,	671-680	(1934).	<i>The significance of chemical bond energies,</i>
		90,	5090-5092	(1968).	<i>Mass spectrometric study of the high-temperature equilibrium <math>C_2F_4 = 2 CF_2</math> and the heat of formation of the <math>CF_2</math> radical,</i>

## 6.6. Oxidized Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Bowers, M.T. and Chau, M., Francisco, J.S. and Goldstein, A.N.,	J. Phys. Chem. Chem. Phys.	80, 127,	1739, 73-79	(1976). (1988).	Some fast fluoride ion transfer reactions of $\text{CO}^+$ with perfluoroalkanes and sulfur hexafluoride. Limits on the heat of formation of $\text{FCO}$ , Dissociation dynamics of $\text{FC(O)O}$ and $\text{ClC(O)O}$ radicals,
Francisco, J.S. and Mina-Camilde, N.,	Can. J. Chem.	71,	135-140	(1993).	A study of hydrogen abstraction reactions by halogen atoms with $\text{HFCO}$ and $\text{HCICO}$ - Determination of transition state structures, barrier heights, and vibrational frequencies,
Francisco, J.S. and Williams, I.H.,	Chem. Phys. Lett.	110,	240	(1984).	Theoretical characterization of the trifluoromethoxy radical,
Francisco, J.S. and Williams, I.H.,	Inter. J. Chem. Kin.	20,	455-466	(1988).	The thermochemistry of polyoxides and poloxyl radicals,
Francisco, J.S. and Zhao, Y.,	Chem. Phys. Lett.	153,	296-302	(1988).	Energetics of the Reactions of $\text{FCO}$ with $\text{O}_2$ using unrestricted Moller-Plesset perturbation theory with spin annihilation,
Francisco, J.S. and Zhao, Y.,	J. Chem. Phys.	93,	276-286	(1990).	The reaction of atomic fluorine with formyl fluoride: An experimental and theoretical study,
Francisco, J.S. and Zhao, Y.,	J. Chem. Phys.	96,	7587-7596	(1992).	Ab initio studies of dissociation pathways on the ground state potential energy surface for $\text{HFCO}$ and $\text{HCICO}$ ,
Francisco, J.S.,	Chem. Phys. Lett.	163,	375-380	(1989).	Decomposition pathways of carbonfluorochloroacetic acid on the ground-state potential energy surface and its implication for a design strategy for alternative halocarbons,
Francisco, J.S.,	J. Atmos. Chem.	16,	285-292	(1992).	A study of the gas-phase reaction of carbonyl fluoride with water,
Francisco, J.S.,	J. Chem. Phys.	96,	7597-7602	(1992).	An examination of substituent effects on the reaction of $\text{OH}$ radical with $\text{HXCO}$ (where X=H,F, and Cl),
Francisco, J.S.,	J. Chem. Soc. Faraday Trans.	88,	3521-3525	(1992).	Decomposition Pathways for Trifluoroacetic Acid, $\text{CF}_3\text{C(O)OH}$ ,
Francisco, J.S.,	J. Chem. Soc. Faraday Trans.	88,	1943-1941	(1992).	Reaction of $\text{OH}$ radical with $\text{CH}_3\text{C(O)H}$ and $\text{CF}_3\text{C(O)H}$ ,
Francisco, J.S., Goldstein, A.N., Li, Z., Zhao, Y., and Williams, I.H.,	J. Phys. Chem.	94,	4791-4795	(1990).	Theoretical investigation of chlorofluorocarbon degradation processes: structures and energetics of $\text{XCl(O)Ox}$ intermediates ( $\text{X} = \text{F}, \text{Cl}$ );
Francisco, J.S., Steinfeld, J.I., Williams, I.H., T.N., and Matula, R.A.,	NBS Spec. Publ.	716,	250-255	(1986).	Thermochemistry, structure and reactivity of the trifluoromethoxy radical,
Gangloff, H.J., Milks, D., Maloney, K.L., Adams, T.N., and Matula, R.A.,	J. Chem. Phys.	63,	4915-4926	(1975).	An experimental and mechanistic study of the reactions of $\text{CO}_2$ with $\text{H}$ and with $\text{CO}$ ,
Goddard, J.D. and Schaefer, H.F., III,	J. Chem. Phys.	93,	4907-4915	(1990).	Formyl fluoride photodissociation: Potential energy surface features of singlet $\text{HFCO}$ ,
Hrusak, J. and Schwarz, H.,	J. Phys. Chem.	97,	4659-4663	(1993).	A GAUSSIAN 1 study of the $[\text{CHO}^+]\text{F}$ potential energy surface - Theoretical evidence for the existence of 3 experimentally distinguishable isomers in the gas phase,
Kamiya, K. and Morokuman, K.,	J. Chem. Phys.	94,	7287-7298	(1991).	Potential energy surface for unimolecular dissociation and rearrangement reactions of the ground electronic state of $\text{HFCO}$ ,
Kerr, J.A.,	Chem. Phys. Lett.	201,	391-392	(1993).	The heat of formation of the $\text{CF}_3\text{CO}$ radical - A note of caution,

## 6.6. Oxidized Fluorocarbon Thermochemistry

Authors	Journal	Issue	Pages	Year	Title
Li, Z.J. and Francisco, J.S.,	<i>Chem. Phys. Lett.</i>	209,	151-160	(1993).	<i>An examination of pathways for the reaction of oxygen atoms with CF3O radicals - implications for the role of CF3 radicals in stratospheric chemical processes,</i>
Maricq, M.M., Szente, J.J., Li, Z., and Francisco, J.S.,	<i>J. Chem. Phys.</i>	98,	784-790	(1993).	<i>Visible absorption spectroscopy of the B2A1-X2B2 transition of fluoriformyl radical, FC(O)O,</i>
Montgomery, J.A. Jr., Michels, H.H., and Francisco, J.S.,	<i>Chem. Phys. Lett.</i>	220,	391-396	(1994).	<i>Ab initio calculation of the heats of formation of CF3OH and CF2O,</i>
Morokuman, K., Kato, S. and Hirao, K.,	<i>J. Chem. Phys.</i>	72,	6800-6802	(1980).	<i>Substitution effect on formaldehyde photochemistry: Potential surface characteristics of HFCO,</i>
Soto, M.R. and Page, M.,	<i>J. Phys. Chem.</i>	94,	3242-3246	(1990).	<i>Features of the potential energy surface for reactions of OH with CH2O,</i>
Sulzle, D., Drewello, T., van Baar, B.L.M., and Schwarz, H.,	<i>J. Am. Chem. Soc.</i>	110,	8330-8333	(1988).	<i>Experimental evidence for the existence of ionized and neutral fluorohydroxymethylene (FCOH) in the gas phase,</i>
Vedeneev, V.I., Gol'denberg, M.Ya., and Teitel'boim, M.A.,	<i>Kinet. Catal.</i>	28,	1055-1059	(1987).	<i>Calculation of the rate constant of the reaction CF3 + O2 = CF3O + O by the transition state method,</i>
Vedeneev, V.I., Teitel'boim, M.A., and Shoikhet, A.A.,	<i>Bull. Acad. Sci. USSR, Div. Chem. Sci.</i>	8,	1534-1537	(1978).	<i>The photolysis of CF3I in the presence of O2 and Br2. I. The mechanism of the elementary step in the reaction of CF3 radicals with O2,</i>
Zhao, Y. and Francisco, J.S.,	<i>Chem. Phys. Lett.</i>	173,	551-556	(1990).	<i>An examination of the heats of formation for the formyl fluoride and formyl chloride (HFCO and HClCO) molecules,</i>
Zhao, Y. and Francisco, J.S.,	<i>Chem. Phys. Lett.</i>	199,	65-70	(1992).	<i>An examination of the reaction pathways for the recombination of FCO radicals,</i>

## 6.7. Fluorocarbon Kinetics (Decompositions)

Authors	Journal	Issue	Pages	Year	Title
Barnes, G.R., Cox, R.A., and Simmons, R.F., Boaglio, D.G., Arbilla, G., Ferrero, J.C., and Staricco, E.H.,	J. Chem. Soc. B Inter. J. Chem. Kin.		1176	(1971).	The kinetics of the gas-phase thermal decomposition of chlorodifluoromethane,
Bryant, J.T. and Pritchard, G.O.,	J. Phys. Chem.	21,	1003-1014	(1990).	Decomposition of 1,1,2,2-tetrafluorocyclopropane. Arrhenius parameters and their influence on the chemical activation results,
Bryant, J.T., Kirtman, B., and Pritchard, G.O.,	J. Phys. Chem.	71,	3439	(1967).	The interactions of methyl and difluoromethyl radicals and the elimination of HF from 'hot' 1,1-difluoroethane,
Bulkovskaya, N.I., Larichev, M.N., Leipunskii, I.O., Morozov, I.I., and Taltroze, V.L.,	Kin. Catal.	21,	1960-1961	(1967).	The elimination of HF from vibrationally excited 1,1,2-trifluoroethane,
Cadman, P., Day, M., and Trotman-Dickenson, A.F.,	J. Chem. Soc. A,		2498-2503	(1970).	Mass-spectrometric study of the recombination of atomic fluorine with CF <sub>3</sub> radicals and CF <sub>2</sub> biradicals,
Cadman, P., Day, M., Kirk, A.W., and Trotman-Dickenson, A.F.,	Chem. Commun.,		203-204	(1970).	Shock tube pyrolyses. Part I. The thermal decomposition of iso-propyl chloride, ethyl fluoride, and n-propyl fluoride,
Cadman, P., Day, M., Trotman-Dickenson, A.F.,	J. Chem. Soc. A		248-252	(1971).	Activation energies for the elimination of hydrogen fluoride from alkyl fluorides obtained by the activated molecule and competitive shock-tube techniques,
Cadman, P., Kirk, A.W., and Trotman-Dickenson, A.F.,	J. Chem. Soc. Faraday Trans. I	72,	1428	(1976).	Shock tube pyrolyses. Part II. Thermal decomposition of isopropyl, n-butyl, isobutyl and t-butyl fluorides,
Cadman, P., Kirk, A.W., and Trotman-Dickenson, A.F.,	J. Phys. Chem.	75,	1625-1631	(1971).	Production of chemically activated fluoroalkanes by direct fluorination, Unimolecular reaction and collisional deactivation of chemically activated 1,2-difluoroethane produced by mercury photosensitization of chlorofluoromethane at 300 and 475 K.
Chang, H.W. and Setser, D.W.,	J. Am. Chem. Soc.	91,	7648-7657	(1969).	Nonequilibrium unimolecular reactions and collisional deactivation of chemically-activated fluoroethane and 1,1,1-trifluoroethane,
Chang, H.W., Craig, N.L., and Setser, D.W.,	J. Phys. Chem.	76,	954-963	(1972).	Mercury-photosensitized photolysis of C <sub>2</sub> F <sub>4</sub> ,
Cohen, N. and Heicklen, J.,	J. Chem. Phys.	43,	871-873	(1965).	Vapour-phase bromination of fluoriform and methane,
Corbett, P., Tarr, A.M. and Whittle, E.,	Trans. Faraday Soc.	59,	1609-1618	(1963).	The kinetics of the gas-phase thermal decomposition of bromodifluoromethane,
Cox, R.A. and Simmons, R.F.,	J. Chem. Soc. B (London)		1625-1631	(1971).	Reactions of I:CX <sub>2</sub> during chlorofluorocarbon pyrolysis,
Day, M. and Trotman-Dickenson, A.F.,	J. Chem. Soc. A, ACS Div. Fuel Chem. Preprints		233-235	(1969).	Kinetics of the thermal decomposition of ethyl fluoride,
DiFelice, J.J. and Ritter, E.R.,	Ind. Eng. Chem. Fundam.	39,	158-161	(1994).	Kinetics of the pyrolysis of chlorodifluoromethane,
Edwards, J.W. and Small, P.A.,	Inter. J. Chem. Kin.	4,	396	(1965).	The unimolecular decomposition of vibrationally excited 1-deuterio-1,1,2-trifluoroethane,
Follmer, D.W. and Pritchard, G.O.,	Theorchem. - J. Mol. Struct.	6,	573-585	(1974).	Thermochemistry of possible degradation pathways for compounds CF <sub>3</sub> CHXY(X, Y = H, F, Cl) using AM1 and MNDO semiempirical methods,
Francisco, J.A., Ghoul, W.A., and Williams, I.H.,	Nature		35-39	(1993).	
Gozzo, F. and Patrick, C.R.,		202,	1329	(1964).	

## 6.7. Fluorocarbon Kinetics (Decompositions)

Authors	Journal	Issue	Pages	Year	Title
Gozzo, F. and Patrick, C.R.,	Tetrahedron	22,	3329-3336	(1966).	The thermal decomposition of chlorodifluoromethane,
Hidaka, Y., Nakamura, T., and Kawano, H.,	Chem. Phys. Lett.	187,	40-44	(1991).	High temperature pyrolysis of CF3H in shock waves,
Jeffers, P. M.,	J. Phys. Chem.	78,	1460-1472	(1974).	Shock Tube Cis-Trans Isomerization Studies. III,
Kerr, J.A. and Timlin, D.M.,	Inter. J. Chem. Kin.	3,	427-441	(1971).	A kinetic study of the thermal elimination of hydrogen fluoride from 1,2-difluoroethane. Determination of the bond dissociation energies D(CH2F-CH2F) and D(CH2F-H).
Kerr, J.A., Kirk, A.W., O'Grady, B.V., Phillips, D.C., Trotman-Dickenson, A.F.,	Disc. Faraday Soc.	44,	263-292	(1967).	Kinetics of decomposition of chemically activated alkyl fluorides,
Kim, K.C., Setser, D.W. and Holmes, B.E.,	J. Phys. Chem.	77,	725-734	(1973).	Hydrogen fluoride and deuterium fluoride elimination reactions of chemically activated 1,1,1-trideuterio, 2,2-difluoroethane, 2,2-difluoroethane, 1,1-difluoroethane and 1,1,1-trideuterio, 2-fluoroethane,
Kirk, A.W., Trotman-Dickenson, A.F., and Trus, B.I.,	J. Chem. Soc. A,		3058-3062	(1968).	The elimination of hydrogen fluoride from chemically activated ethyl fluoride as a function of energy,
Kochubei, V.F., Gavriliv, A.P., Moin, F.B., and Pazderskii, Yu. A.,	Kin. Catal.	21,	558	(1980).	Reaction kinetics of thermal 1,1-difluoroethane decomposition,
Kushina, I.D., Belfermer, A.I., and Shevchuk, V.U.,	Kin. Catal.	13,	758-764	(1972).	Kinetic regularities of the thermal transformation of dichlorofluoromethane,
Millward, G.E. and Tschuikow-Roux, E.,	J. Phys. Chem.	76,	292-298	(1972).	A kinetic analysis of the shock wave decomposition of 1,1,1,2-tetrafluoroethane,
Millward, G.E., Hartig, R., and Tschuikow-Roux, E.,	Chem. Commun.,		465-466	(1971).	Hydrogen fluoride elimination from shock-heated 1,1,2,2-tetrafluoroethane,
Millward, G.E., Hartig, R., and Tschuikow-Roux, J. Phys. Chem.		75,	3195-3201	(1971).	Kinetics of the shock wave thermolysis of 1,1,2,2-tetrafluoroethane,
Mitin, P.V., Barabanov, V.G., and Volkov, G.V.,	Kin. Catal.	29,	1279	(1988).	Kinetics of the thermal decomposition of 1,1-difluoro-1-chloroethane and 1,1,1-trifluoroethane,
Modica, A.P. and LaGraff, J.E.,	J. Chem. Phys.	43,	3383-3392	(1965).	Decomposition and oxidation of C2F4 behind shock waves,
Modica, A.P. and LaGraff, J.E.,	J. Chem. Phys.	45,	4729-4733	(1966).	C2F4 dissociation in nitrogen shocks,
Modica, A.P. and LaGraff, J.E.,	J. Chem. Phys.	44,	3375-3379	(1966).	Mass-spectrometer and uv absorption study of CHF3 decomposition behind shock waves,
Modica, A.P. and Sillers, S.J.,	J. Chem. Phys.	48,	3283-3289	(1968).	Experimental and theoretical kinetics of high temperature fluorocarbon chemistry,
Perona, M.J., Bryant, J.T., and Pritchard, G.O.,	J. Am. Chem. Soc.	90,	4782-4786	(1968).	The decomposition of vibrationally excited 1,1,1-trideutrio-2,2-difluoroethane,
Phillips, D.C. and Trotman-Dickenson, A.F.,	J. Chem. Soc. A,		1144-1149	(1968).	The kinetics of the elimination of hydrogen fluoride from chemically activated 1,1,2-trifluoroethane and 1,1,2,2-tetrafluoroethane,
Plumb, I.C. and Ryan, K.R.,	Ber. Bunsenges. Phys. Chem.	6,		(1986).	Gas-phase reactions of CF3 and CF2 with atomic and molecular fluorine: their significance,

## 6.7. Fluorocarbon Kinetics (Decompositions)

Authors	Journal	Issue	Pages	Year	Title
Politanskii, S.F. and Shevchuk, U.V.,	<i>Kin. Catal.</i>	9,	411-417	(1968).	<i>Thermal conversions of fluoromethanes. II. Pyrolysis of difluoromethane and trifluoromethane,</i>
Pritchard, G.O. and Perona, M.J.,	<i>Inter. J. Chem. Kin.</i>	2,	281-297	(1970).	<i>The elimination of HF from vibrationally excited fluoroethanes. The decomposition of 1,1,1-trifluoroethane-d0 and d3,</i>
Pritchard, G.O. and Thommarson, R.L.,	<i>J. Phys. Chem.</i>	71,	1674-1682	(1967).	<i>The photolysis of fluoroacetone and the elimination of hydrogen fluoride from 'hot' fluoroethanes,</i>
Pritchard, G.O., Venugopalan, M., Graham, T.F.,	<i>J. Phys. Chem.</i>	68,	1786	(1964).	<i>Photochemistry of the fluoro ketones. The production of vinyl fluoride in the photolysis of 1,3-difluoroacetone,</i>
Rodgers, A.S. and Ford, W.G.F.,	<i>Inter. J. Chem. Kin.</i>	5,	965-975	(1973).	<i>Analysis of the kinetics of the thermal and chemically activated elimination of HF from 1,1,1-trifluoroethane. The C-C bond dissociation energy and the heat of formation of 1,1,1-trifluoroethane,</i>
Schug, K.P. and Wagner, H.Gg.,	<i>Ber. Bunsenges. Phys. Chem.</i>	82,	719-725	(1978).	<i>Der thermische zerfall von C2F4 in der gasphase. Zur bildungsenthalpie von difluorcarbenen,</i>
Schug, K.P. and Wagner, H.Gg.,	<i>Z. Phys. Chem.</i>	86,	59-66	(1973).	<i>Zum thermischen Zerfall von CH3F.</i>
Schug, K.P., Wagner, H.Gg., and Zabel, F.,	<i>Ber. Bunsenges. Phys. Chem.</i>	83,	167	(1979).	<i>Gas phase elimination of hydrogen halides from halomethanes. I. Thermal decomposition of chlorodifluoromethane, trifluoromethane, and trichloromethane behind shock waves.</i>
Sekhar, M.V.C. and Tschukow-Roux, E.,	<i>J. Phys. Chem.</i>	78,	472-477	(1974).	<i>Kinetics of the shock-induced competitive dehydrofluorinations of 1,1,2-trifluoroethane,</i>
Simmie, J.M. and Tschukow-Roux, E.,	<i>Chem. Commun.</i>		773	(1970).	<i>Thermal decomposition of vinylidene fluoride behind reflected shock waves,</i>
Simmie, J.M. and Tschukow-Roux, E.,	<i>J. Phys. Chem.</i>	74,	4075-4079	(1970).	<i>Kinetics of the shock-initiated decomposition of 1,1-difluorethylene,</i>
Simmie, J.M., Quiring, W.J., and Tschukow-Roux, E.,	<i>J. Phys. Chem.</i>	73,	3830-3833	(1969).	<i>The thermal decomposition of perfluoroclobutane in a single-pulse shock tube,</i>
Simmie, J.M., Quiring, W.J., and Tschukow-Roux, E.,	<i>J. Phys. Chem.</i>	74,	992-994	(1970).	<i>Kinetics of the dehydrofluorination of vinyl fluoride in a single-pulse shock tube,</i>
Tsang, W.,	<i>J. Phys. Chem.</i>	90,	414-418	(1986).	<i>Single pulse shock tube study on the stability of perfluorobromoethane,</i>
Tschukow-Roux, E. and Marte, J.E.,	<i>J. Chem. Phys.</i>	42,	2049-2056	(1965).	<i>Thermal decomposition of fluoroform in a single pulse shock tube. I.</i>
Tschukow-Roux, E. and Quiring, W.J.,	<i>J. Phys. Chem.</i>	75,	295-300	(1971).	<i>Kinetics of the thermally induced dehydrofluorination of 1,1,1-trifluoroethane in shock waves,</i>
Tschukow-Roux, E.,	<i>J. Chem. Phys.</i>	43,	2251-2256	(1965).	<i>Kinetics of the thermal decomposition of C2F6 in the presence of H2 at 1300-1600K,</i>
Tschukow-Roux, E.,	<i>J. Chem. Phys.</i>	42,	3639-3642	(1965).	<i>Thermal decomposition of fluorofrom in a single-pulse shock tube. II.</i>
Tschukow-Roux, E., Millward, G.E., and Quiring, W.J.,	<i>J. Phys. Chem.</i>	75,	3493-3498	(1971).	<i>Kinetics of the shock wave pyrolysis of pentfluoroethane,</i>
Tschukow-Roux, E., Quiring, W.J., and Simmie, J.M.,	<i>J. Phys. Chem.</i>	74,	2449-2455	(1970).	<i>Kinetics of the thermal decomposition of 1,1-difluoroethane in shock waves. A consecutive first-order reaction,</i>

### 6.7. Fluorocarbon Kinetics (Decompositions)

Authors	Journal	Issue	Pages	Year	Title
Zimbov, K.F., Uy, O.M., and Margrave, J.L.	<i>J. Am. Chem. Soc.</i>	90,	5090-5092	(1968).	<i>Mass spectrometric study of the high-temperature equilibrium C2F4 = 2 CF2 and the heat of formation of the CF2 radical,</i>

## 6.8. Fluorocarbon Kinetics (Abstractions)

Authors	Journal	Issue	Pages	Year	Title
Aders, W.-K., Pangritz, D.,, and Wagner, H.Gg.,	Ber. Bunsenges. Phys. Chem.	79,	90	(1975).	Untersuchungen zur reaktion von wasserstoffatomen mit methyfluoride, methylchlorid und methylbromid,
Alocock, W.G. and Whittle, E.,	J. Chem. Soc. Faraday Trans.	61,	244	(1965).	Reactions of trifluoromethyl radicals with organic halides. Part I - Methyl halides
Amphlett, J.C. and Whittle, E.,	Trans. Faraday Soc.	63,	2695	(1967).	Reactions of trifluoromethyl radicals with iodine and hydrogen iodide,
African, H., and Arthur, N.L.,	Inter. J. Chem. Kin.	18,	437-443	(1986).	Reaction of CF3 radicals with C2H6,
Arthur, N.L. and Bell, T.N.,	Can. J. Chem.	44,	1445	(1966).	Kinetics of the abstraction of hydrogen atoms from hydrogen sulfide by trifluoromethyl radicals,
Arthur, N.L. and Bell, T.N.,	Rev. Chem. Intermed.	2,	37-74	(1978).	An evaluation of the kinetic data for hydrogen abstraction from silanes in the gas phase,
Arthur, N.L., Donchi, K.F., and McDonell, J.A.,	J. Chem. Soc. Faraday Trans.	71,	2431	(1975).	REBO calculations. Part 4. - Arrhenius parameters and kinetic isotope effects for the reactions of CH3 and CF3 radicals with H2 and D2,
Ayscough, P.B. and Polanyi, J.C.,	Trans. Faraday Soc.	52,	960-970	(1956).	The reactions of trifluoromethyl radicals with hydrogen isotopes,
Ayscough, P.B., Polanyi, J.C., and Steacie, E.W.R.,	Can. J. Chem.	33,	743	(1955).	The vapor phase photolysis of hexafluoroacetone in the presence of methane and ethane,
Bassett, J.E. and Whittle, E.,	J. Chem. Soc. Faraday Trans. 1	68,	492-498	(1972).	Reaction of C2F5 radicals with HCl. Determination of the bond dissociation energy D(C2F5-H).
Bottoni, A., Poggi, G., and Emmi, S.S.,	J. Mol. Struct. (Theochem)	279,	299-309	(1993).	An ab initio study of H abstraction in halogen-substituted methanes by the OH radical.
Bradley, J. N., Capey, W. D., Fair, R. W. and Pritchard, D. K.,	Inter. J. Chem. Kin.	8,	549-561	(1976).	A shock-tube study of the kinetics of reaction of hydroxyl radicals with H2, CO, CH4, CF3H, C2H4 and C2H6,
Cadman, P., Kirk, A.W., and Trotman-Dickenson, A.F.,	J. Chem. Soc. Chem. Comm.	72,	1027	(1976).	Reactions of chlorine atoms with ethane, propane, isobutane, fluoroethane, 1,1-difluoroethane, 1,1-trifluoroethane, and cyclopropane,
Carlton, T.S., Steeper, J.R., and Christensen, R.L.,	J. Phys. Chem.	70,	3222	(1966).	Rates of hydrogen abstraction from methanol by CF3 radicals,,
Carmichael, H. and Johnston, H.S.,	J. Chem. Phys.	41,	1975-1982	(1964).	Correlation of activation energies and bond energies in CF3 reactions, On the question of negative activation energies; absolute rate constants by RRKM and GI theory for CH3 + HX CH4 + X (X = Cl, Br)
Chen, Y., Rauk, A., and Tschukow-Roux, E.,	J. Chem. Phys.	95,	9900-9908	(1991).	Atmospheric chemistry - Rate constants of the gas-phase reactions between halalkanes of environmental interest and hydroxyl radicals,
Chiorboli, C., Piazza, R., Tosato, M.L., Carassiti, V.,	Coord. Chem. Rev.	125,	241-250	(1993).	Reaction kinetics involving ground and excited hydroxyl radicals. Part
Clyne, M.A.A. and Holt, P.M.,	Ber. Bunsenges. Phys. Chem.	75,	?+L159582	(1979).	2 - Rate constants for reactions of ground state OH with halogenomethanes and halogenoethanes,
Clyne, M.A.A. and Holt, P.M.,	J. Chem. Soc. Faraday Trans. 2	75,	582	(1979).	Reaction kinetics involving ground and excited hydroxyl radicals. Part 2 - Rate constants for reactions of ground state OH with halogenomethanes and halogenoethanes,
Clyne, M.A.A., McKenney, D.J., and Walker, R.F.,	Can. J. Chem.	51,	3596	(1973).	Reaction kinetics of ground state fluorine F(2P) atoms. I. Measurement of fluorine atom concentrations and the rates of reactions of F + CHF3 and F + Cl2 using mass spectrometry.

## 6.8. Fluorocarbon Kinetics (Abstractions)

Authors	Journal	Issue	Pages	Year	Title
Cohen, N. and Benson, S.W.,	<i>J. Phys. Chem.</i>	91,	171-175	(1987).	<i>Empirical correlations for rate coefficients for reactions of OH with haloalkanes,</i>
Cohen, N. and Benson, S.W.,	<i>J. Phys. Chem.</i>	91,	162-170	(1987).	<i>Transition-state-theory calculations for reactions of OH with haloalkanes,</i>
Fagarash, M.B. and Moin, F.B.,	<i>Kinet. Catal.</i>	9,	1135	(1968).	<i>Kinetics of the reaction of the CF<sub>3</sub> radical with ammonia,</i>
Fox, G.L. and Schlegel, H.B.,	<i>J. Phys. Chem.</i>	96,	298-302	(1992).	<i>An ab initio study of hydrogen atom abstractions from substituted methanes by substituted methyl radicals,</i>
Gierczak, T., Talukdar, R., Vaghjiani, G.L.,	<i>J. Geophys. Res.</i>	96,	5001-5011	(1991).	<i>Atmospheric fate of hydrofluoroethanes and hydrofluorochloroethanes: I. Rate coefficients for reactions with OH,</i>
Lovejoy, E.R., and Ravishankara, A.R.,	<i>Trans. Faraday Soc.</i>	63,	662-672	(1967).	<i>Reactions of trifluoromethyl radicals with organic halides. Part 5.- Fluoromethanes and fluoroethanes,</i>
Giles, R.D., Quick, L.M., and Whittle, E.,	<i>Ber. Bunsenges. Phys. Chem.</i>	82,	1161-1166	(1978).	<i>Kinetics of the reactions of OH radicals with some halocarbons (CHClF<sub>2</sub>, CH<sub>2</sub>ClF, CH<sub>2</sub>ClCF<sub>3</sub>, CH<sub>3</sub>CClF<sub>2</sub>, CH<sub>3</sub>CHF<sub>2</sub>) in the temperature range 260-370 K,</i>
Handwerk, V. and Zellner, R.,	<i>J. Chem. Phys.</i>	64,	197-202	(1976).	<i>Rate constants for the reactions of OH with CH<sub>4</sub> and fluorine, chlorine, and bromine substituted methanes at 296 K,</i>
Howard, C.J. and Evenson, K.M.,	<i>J. Chem. Phys.</i>	64,	4303	(1976).	<i>Rate constants for the reactions of OH with ethane and some halogen substituted ethanes at 269 K,</i>
Howard, C.J. and Evenson, K.M.,	<i>J. Phys. Chem.</i>	86,	1808-1815	(1982).	<i>Cl- and F-substituted methanes. 1. Experimental results, comparisons, and applications,</i>
Jeong, K.-M. and Kaufmann, F.,	<i>J. Phys. Chem.</i>	86,	1816-1821	(1982).	<i>Cl- and F-substituted methanes. 2. Calculation of rate parameters as a test of transition-state theory,</i>
Jeong, K.-M. and Kaufmann, F.,	<i>J. Phys. Chem.</i>	83,	1222	(1984).	<i>Kinetics of the reactions of OH with C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>CCl<sub>3</sub>, CH<sub>2</sub>ClCHCl<sub>2</sub>, CH<sub>2</sub>ClCCl<sub>2</sub>, and CH<sub>2</sub>FCF<sub>3</sub>,</i>
Kaufmann, F.J.,	<i>J. Chim. Phys.</i>	75,	318	(1978).	<i>Etude cinétique des réactions du 1,1,1-trifluoro, 2-chloroethane avec les atomes de chlore et d'oxygène,</i>
Jourdain, J.-L., Le Bras, G., and Combourieu, J.,	<i>Inter. J. Chem. Kin.</i>	3,	69-84	(1971).	<i>Hydrogen abstraction from organosilicon compounds. The reactions of fluoromethyl radicals with tetramethylsilane. Polar effects in gas phase reactions,</i>
Kerr, J.A. and Timlin, D.M.,	<i>J. Chem. Phys.</i>	49,	4825	(1968).	<i>Photolysis of hexafluoroacetone in the presence of H<sub>2</sub>, D<sub>2</sub>, and HD. Kinetic isotope effects in the reaction of CF<sub>3</sub> with molecular hydrogen,</i>
Kibby, C.L. and Weston, R.E., Jr.,	<i>Kin. Catal.</i>	10,	405	(1969).	<i>Kinetics of the reaction of CF<sub>4</sub> with hydrogen,</i>
Kochubei, V.F. and Moin, F.B.,	<i>Kin. Catal.</i>	11,	712	(1971).	<i>Kinetics of high-temperature reaction of atomic hydrogen with CO<sub>2</sub> and CF<sub>4</sub>,</i>
Laurence, G.S.,	<i>Trans. Faraday Soc.</i>	63,	1155-1165	(1967).	<i>Thermal and photochemical exchange of iodide with trifluoro-methyl iodide,</i>
Liu, R., Huie, R.E., and Kurylo, M.J.,	<i>J. Phys. Chem.</i>	94,	3247-3249	(1990).	<i>Rate constants for the reactions of the OH radical with some hydrochlorofluorocarbons over the temperature range 270-400 K,</i>

## 6.8. Fluorocarbon Kinetics (Abstracts)

Authors	Journal	Issue	Pages	Year	Title
Martin, J.-P. and Paraskevopoulos, G.,	<i>Can. J. Chem.</i>	61,	861	(1983).	<i>A kinetics study of the reactions of OH radicals with fluorocarbons. Estimates of C-H bond strength in fluorokanes,</i>
Miyoshi, A., Ohmori, K., Tsuchiya, K., and Matsui, H.,	<i>Chem. Phys. Lett.</i>	204,	241-247	(1993).	<i>Reaction rates of atomic oxygen with straight chain alkanes and fluoromethanes at high temperatures,</i>
Mo, S.-H., Grant, E.R., Little, F.E., Manning, R.G., Mathis, C.A., Werre, G.S., and Root, J.W.,	<i>ACS Symp. Ser.</i>	66,	59-103	(1978).	<i>Radiotracer studies of thermal hydrogen abstraction reactions by atomic fluorine,</i>
Morris, E.R. and Thynne, J.C.J.,	<i>Trans. Faraday Soc.</i>	64,	414-427	(1968).	<i>Reactions of radicals containing fluorine. Part I: Hydrogen and deuterium atoms abstraction from trideuteriomethanol by trifluoromethyl radicals,</i>
Nielsen, O.J.,	<i>Chem. Phys. Lett.</i>	187,	286-290	(1991).	<i>Rate constants for the gas-phase reactions of OH radicals with CH<sub>3</sub>CHF<sub>2</sub> and CHCl<sub>2</sub>CF<sub>3</sub> over the temperature range 295-388 K, and CH<sub>3</sub>CHF<sub>2</sub> at 297 K,</i>
Nip, W.S., Singleton, D.L., Overend, R., and Paraskevopoulos, G.,	<i>J. Phys. Chem.</i>	83,	2440-2443	(1979).	<i>Rates of OH radical reactions with CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub>, CHF<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>F, and CH<sub>3</sub>CHF<sub>2</sub> at 297 K,</i>
Orkin, V.L. and Khamaganov, V.G.,	<i>J. Atmos. Chem.</i>	16,	157	(1993).	<i>Determination of Rate Constants for Reactions of Some Halocarbons with OH Radicals and their Atmospheric Lifetimes,</i>
Orkin, V.L. and Khamaganov, V.G.,	<i>J. Atmos. Chem.</i>	16,	169	(1993).	<i>Rate Constants for Reactions of OH with Some Br-Containing Halokanes,</i>
Pagsberg, P., Munk, J., Sillesen, A., and Anastasi, Paraskevopoulos, G., Singleton, D.L., and Irwin, R.S.,	<i>Chem. Phys. Lett.</i>	146,	375-381	(1988).	<i>UV spectrum and kinetics of hydroxymethyl radicals, Rates of OH radical reactions. 8. Reactions with CH<sub>2</sub>FCl, CH<sub>2</sub>Cl<sub>2</sub>, CHFCl<sub>2</sub>, CH<sub>3</sub>CF<sub>3</sub>Cl, CH<sub>3</sub>Cl, and C<sub>2</sub>H<sub>5</sub>Cl at 297 K,</i>
Parsamyan, N.I. and Nalbandyan, A.B.,	<i>Arm. Khim. Zh.</i>	21,	1	(1968).	<i>Determination of the rate constants for reactions of hydrogen and oxygen atoms with difluoromethane,</i>
Parsamyan, N.I., Azatyan, V.V., and Nalbandyan, A.B.,	<i>Arm. Khim. Zh.</i>	20,	1	(1967).	<i>Determination of the rate constant for reaction of atomic hydrogen and oxygen with methyl fluoride,</i>
Perry, R.A., Atkinson, R. and Pitts, J.N., Jr.,	<i>J. Chem. Phys.</i>	67,	458-462	(1977).	<i>Rate constants for the reaction of OH radicals with CH<sub>2</sub>=CHF, CH<sub>2</sub>=CHCl, and CH<sub>2</sub>=CHBr over the temperature range 299-426 K,</i>
Pickard, J.M. and Rodgers, A.S.,	<i>Inter. J. Chem. Kin.</i>	15,	569-577	(1983).	<i>Kinetics of the gas phase reaction CH<sub>3</sub>F + I<sub>2</sub> = CH<sub>2</sub>FI + HI: The C-H bond dissociation energy in methyl and methylene fluorides,</i>
Pickard, J.M. and Rodgers, A.S.,	<i>J. Am. Chem. Soc.</i>	99,	691-694	(1977).	<i>The kinetics and thermochemistry of the reaction of 1,1-difluoroethane with iodine. The CF<sub>2</sub>-H bond dissociation energy in 1,1-difluoroethane and the heat of formation of 1,1-difluoroethyl,</i>
Pritchard, G.O. and Miller, G.H.,	<i>J. Chem. Phys.</i>	35,	1135-1136	(1961).	<i>Comparison of CH<sub>3</sub> and CF<sub>3</sub> hydrogen abstraction reaction,</i>
Pritchard, G.O. and Perona, M.J.,	<i>Inter. J. Chem. Kin.</i>	1,	509-525	(1969).	<i>Some hydrogen atom abstraction reactions of CF<sub>2</sub>H and CFH<sub>2</sub> radicals, and the C-H bond dissociation energy in CF<sub>2</sub>H<sub>2</sub>,</i>
Pritchard, G.O., Dacey, J.R., Kent, W.C., and Simonds, C.R.,	<i>Can. J. Chem.</i>	44,	171	(1966).	<i>Some hydrogen abstraction reactions of perfluoroethyl radicals,</i>
Pritchard, G.O., Pritchard, H.O., Schiff, H.I., and Trotman-Dickenson, A.F.,	<i>Trans. Faraday Soc.</i>	52,	849	(1956).	<i>The reactions of trifluoromethyl radicals,</i>

## 6.8. Fluorocarbon Kinetics (Abstractions)

Authors	Journal	Issue	Pages	Year	Title
Quick, L.M. and Whittle, E.,	<i>Trans. Faraday Soc.</i>	67,	1727-1738	(1971).	<i>Reactions of trifluoromethyl radicals with organic halides. Part 6.-bromo- and fluoro-bromoethanes,</i>
Raal, F.A. and Steacie, E.W.R.,	<i>J. Chem. Phys.</i>	20,	578-581	(1952).	<i>The reaction of methyl radicals with some halozenated methanes,</i>
Richter, H., Vandooren, J., Van Tiggelen, P.J.,	<i>J. Chim. Phys.</i>	91,	1748-1762	(1994).	<i>Kinetics of the consumption of CF<sub>3</sub>H, CF<sub>2</sub>HCl, and CF<sub>2</sub>O in H<sub>2</sub>/O<sub>2</sub> flames,</i>
Ridley, B.A., Davenport, J.A., Stief, L.J., and	<i>J. Chem. Phys.</i>	57,		(1972).	<i>Absolute Rate Constant for the Reaction H + H<sub>2</sub>CO,</i>
Welge, K.H.,					
Singletor, D.L., Paraskevopoulos, G., and Irwin,	<i>J. Phys. Chem.</i>	84,	2339	(1980).	<i>Reaction of OH with CH<sub>3</sub>CH<sub>2</sub>F. The extent of H abstraction from the alpha and beta positions,</i>
R.S.,					
Smith, D.J., Selser, D.W., Kim, K.C., and Bogan,	<i>J. Phys. Chem.</i>	81,	898	(1977).	<i>Relative rate constants for hydrogen abstraction from hydrocarbons, substituted methanes, and inorganic hydrides,</i>
Talukdar, R., Mellouki, A., Gierczak, T.,	<i>J. Phys. Chem.</i>	95,	5815-5821	(1991).	<i>Atmospheric fate of CF<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>CF<sub>3</sub>, CHF<sub>2</sub>CF<sub>3</sub>, and CH<sub>3</sub>CFC<sub>2</sub>: Rate coefficients for reactions with OH and UV absorption cross sections of CH<sub>3</sub>CFC<sub>2</sub>,</i>
Burkholder, J.B., McKeen, S.A., and					
Ravishankara, A.R.,					
Tomkinson, D.M. and Pritchard, H.O.,	<i>J. Phys. Chem.</i>	70,	1579	(1966).	<i>Abstraction of halogen atoms by methyl radicals,</i>
Tschukow-Roux, E., Salomon, and Paddison, S.,	<i>J. Phys. Chem.</i>	91,	3037-3040	(1987).	<i>Reaction of atomic bromine with ethyl bromide. The heat of formation of the CH<sub>3</sub>CHBr radical and the carbon-hydrogen bond dissociation energy;</i>
Westenberg, A.A. and deHaas, N.,	<i>J. Chem. Phys.</i>	62,	3321-3325	(1975).	<i>Rates of H + CH<sub>3</sub>X reactions,</i>
Zhang, Z., Saini, R.D., Kurylo, M.J., and Huie,	<i>Chem. Phys. Lett.</i>	200,	230-234	(1992).	<i>Rate Constants for the Reactions of the Hydroxyl Radical with CH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CHF<sub>2</sub> and CF<sub>3</sub>CHFCHFCF<sub>2</sub>CF<sub>3</sub>,</i>
R.E.,					
Zhang, Z., Saini, R.D., Kurylo, M.J., and Huie,	<i>J. Phys. Chem.</i>	96,	9301-9304	(1992).	<i>Rate Constants for the Reactions of the Hydroxyl Radical with Several Partially Fluorinated Ethers,</i>
R.E.,					

## 6.9. Fluorocarbon Kinetics (Oxidations)

Authors	Journal	Issue	Pages	Year	Title
Atkinson, R. and Pitts, J.N., Jr.,	<i>J. Chem. Phys.</i>	67,	2488-2491	(1977).	Rate constants for the reaction of $O(3P)$ atoms with $CH_2=CHF$ , $CH_2=CHCl$ , and $CH_2=CHBr$ over the temperature range 298-442 K,
Bauer, S.H., Hou, K.C., and Resler, E.I., Jr.,	<i>The Phys. of Fluids, Suppl. I,</i>	12,	125	(1969).	Single-pulse shock-tube studies of the pyrolysis of fluorocarbons and of the oxidation of perfluoroethylene,
Caralp, F., Lesclaux, R., and Dognon, A.M.,	<i>Chem. Phys. Lett.</i>	129,	433-438	(1986).	Kinetics of the reaction of $CF_3$ with $O_2$ over the temperature range 233-
Cohen, N. and Heicklen, J.,	<i>J. Phys. Chem.</i>	70,	3082-3088	(1966).	The production of perfluorocyclopropane in the reaction of oxygen atoms with tetrafluoroethylene,
Cookson, J.L., Hancock, G., and McKendrick, K.G.,	<i>Ber. Bunsenges. Phys. Chem.</i>	89,	335-336	(1985).	Reactions of $CHF(XIA')$ and $NCO(X2\delta)$ radicals,
Cooper, R., Cumming, J.B., Gordon, S., and Mulac, W.A.,	<i>Radiat. Phys. Chem.</i>	16,	169	(1980).	The reactions of the halomethyl radicals $CCl_3$ and $CF_3$ with oxygen,
Cvetanovic, R.J.,	<i>J. Phys. Chem. Ref. Data</i>	16,	261-302	(1987).	Evaluated chemical kinetic data for the reactions of atomic oxygen $O(3P)$ with unsaturated hydrocarbons,
Gilbert, J.R., Slagle, I.R., Graham, R.E., and Gutman, D.,	<i>J. Phys. Chem.</i>	80,	14-18	(1976).	Direct identification of reactive routes and measurement of rate constants in the reactions of oxygen atoms with the fluoroethylenes,
Gordon, R.J. and Lin, M.C.,	<i>Chem. Phys. Lett.</i>	22,	107-118	(1973).	Chemical HF laser emission from the $CHF + O_2$ reaction,
Hancock, G., Harrison, P.D., and MacRobert, A.J.,	<i>J. Chem. Soc. Faraday Trans. 2</i>	82,	647-651	(1986).	Rate-constant measurement of the $O(3P) + CF_2$ ( $X1A'$ ) reaction,
Hancock, G., Ketley, G.W. and MacRobert, A.J.,	<i>J. Phys. Chem.</i>	88,	2104-2109	(1984).	$CHF(XIA')$ radical kinetics. 2. Reaction with $O$ and $N$ atoms,
Heicklen, J., Knight, V.,	<i>J. Phys. Chem.</i>	70,	3893	(1966).	Reaction of oxygen atoms with tetrafluoroethylene in the presence of molecular oxygen,
Herron, J.T. and Huie, R.E.,	<i>J. Phys. Chem. Ref. Data</i>	2,	467-518	(1973).	Rate constants for the reactions of atomic oxygen ( $O(3P)$ ) with organic compounds in the gas phase,
Herron, J.T.,	<i>J. Phys. Chem. Ref. Data</i>	17,	967	(1988).	Evaluated chemical kinetic data for the reactions of atomic oxygen $O(3P)$ with saturated organic compounds in the gas phase,
Jones, D.S. and Moss, S.J.,	<i>Inter. J. Chem. Kin.</i>	6,	443-452	(1974).	Arrhenius parameters for reactions of oxygen atoms with the fluorinated ethylenes,
Jones, S. and Whittle, E.,	<i>Can. J. Chem.</i>	48,	3601	(1970).	Reactions of trifluoromethyl and methyl radicals with ethylene oxide,
Kaiser, E.W.,	<i>Inter. J. Chem. Kin.</i>	25,	667-680	(1993).	Relative rate constants for reactions of $HFC-152a$ , $HFC-143$ , $HFC-143a$ , $HFC-134a$ , and $HFC-124$ with F-atoms or Cl-atoms and for $CF2CH_3$ , $CF2HCH_2$ , and $CF3CFH$ radicals with $F_2$ , $Cl_2$ , and $O_2$ ,
Keating, E.I. and Matula, R.A.,	<i>J. Chem. Phys.</i>	66,	1237-1244	(1977).	The high temperature oxidation of tetrafluoroethylene,
Lenzi, M. and Mele, A.,	<i>J. Chem. Phys.</i>	43,	1974	(1965).	Kinetics of the thermal decomposition of tetrafluoroethylene oxide,
Li, Z.J. and Francisco, J.S.,	<i>Chem. Phys. Lett.</i>	209,	151-160	(1993).	An examination of pathways for the reaction of oxygen atoms with $CF_3O$ radicals - implications for the role of $CF_3$ radicals in stratospheric chemical processes,
Lin, M.C.,	<i>Inter. J. Chem. Kin.</i>	5,	173-176	(1973).	Chemical lasers produced from $O(3P)$ atom reactions. I. Observation of $CO$ and $HF$ laser emissions from several O atom reactions,

## 6.9. Fluorocarbon Kinetics (Oxidations)

Authors	Journal	Issue	Pages	Year	Title
Lin, M.C.,	J. Phys. Chem.	75,	3642-3644	(1975).	Chemical lasers produced from O(1D) atom reactions from the O(1D) + CH <sub>n</sub> F <sub>4-n</sub> (n=1,2, and 3) reactions,
Mahmud, K., Marshall, P., and Fontijn, A.,	J. Phys. Chem.	91,	1568-1573	(1987).	A high-temperature photochemistry kinetics study of the reaction of O(3P) atoms with ethylene from 290-1510 K,
Maricq, M.M. and Szente, J.J.,	J. Phys. Chem.	96,	4925-4930	(1992).	Flash photolysis-time-resolved UV absorption study of the reactions CF3H + F CF3 + HF and CF3 + O2 CF3O2 Products,
Maricq, M.M., Szente, J.J., and Kaiser, E.W.,	Chem. Phys. Lett.	197,	149-156	(1992).	A Kinetic Study of the CF3CFH Recombination and O2 Addition Reactions,
Mitchell, R.C. and Simons, J.P.,	J. Chem. Soc. B,		1005-1007	(1968).	The reaction of O(3P) atoms with 1,1-difluoro-olefins,
Nielsen, O.J., Munk, J., Locke, G., and Wallington, T.J.,	J. Phys. Chem.	95,	8714-8719	(1991).	Ultraviolet absorption spectra and kinetics of the self-reaction of CH2Br and CH2Br-O radicals in the gas phase at 298 K,
Park, J.-Y., Sawyer, P.F., Heaven, M.C., and Gutman, D.,	J. Phys. Chem.	99,	2821-2837	(1984).	Chemical branching in the oxygen-atom-reaction with vinyl fluoride. Pressure dependence of the route O + C2H3F CH2F + HCO,
Peeters, J. and Van Hoeymissen, J.,	J. Phys. Chem.	96,	1257-1263	(1992).	Absolute rate constant measurements of CF(XIP) reactions. I. Reactions with O2, F2, Cl2, and NO,
Vanhaelemeersch, S., and Verheylen, D.,	Plasma Chem. Plasma Process	6,	205	(1986).	A model of the chemical processes occurring in CF4/O2 discharges used in plasma etching,
Plumb, I.C. and Ryan, K.R.,	Plasma Chem. Plasma Process	86,	4678-4683	(1982).	Kinetics of the reactions of CF3 with O(3P) and O2 at 295 K.
Ryan, K.R. and Plumb, I.C.,	Plasma Chem. Plasma Proc.	4,	271	(1984).	Gas-phase reactions of CF2 with O(3P) to produce COF: their significance in plasma processing,
Saunders, D. and Heicklen, J.,	J. Am. Chem. Soc.	87,	2088	(1965).	The reaction of oxygen atoms with tetrafluoroethylene,
Saunders, D. and Heicklen, J.,	J. Phys. Chem.	70,	1950-1958	(1966).	Some reactions of oxygen atoms. I. C2F4, C3F6, C2H2, C2H4, C3H6, 1-C4H8, C2H6, c-C3H6, C3H8,
Slagle, I.R., Gutman, D., and Gilbert, J.R.,	Symp. Int. Combust.	15,	785-793	(1974).	Direct identification of products and measurement of branching ratios for the reactions of oxygen atoms with vinylfluoride, vinylchloride, and vinylbromide,
Teitelboim, M.A. and Vedeneev, V.I.,	Kin. Catal.	26,	1119	(1986).	Rate constants of reactions of trifluoromethyl radicals with oxygen and fluorine,
Tsai, C. and McFadden, D.L.,	J. Phys. Chem.	94,	3298-3300	(1990).	Gas-phase atom-radical kinetics of atomic hydrogen, nitrogen, and oxygen reactions with CHF radicals,
Tsai, C., Belanger, S.M., Kim, J.T., Lord, J.R., and McFadden, D.L.,	J. Phys. Chem.	93,	1916-1922	(1989).	Gas-phase atom-radical kinetics of elementary CF3 reactions with O and N atoms,
Tsai, C.-P. and McFadden, D.L.,	Chem. Phys. Lett.	173,	241-244	(1990).	Gas-phase atom-radical kinetics of N and O atoms reactions with CF and CF2 radicals,
Tyerman, W.J.R.,	Trans. Faraday Soc.	65,	163	(1969).	Rate parameters for reaction of oxygen atoms with C2F4, CF2FCl and CF2CCl2,
Umemoto, H., Sugiyama, K., Tsunashima, S., and Sato, S.,	Bull. Chem. Soc. Jpn.	58,	1228	(1985).	The Arrhenius parameters for the reactions of O atoms with ethene and five fluoroethenes,

## 6.9. Fluorocarbon Kinetics (Oxidations)

Authors	Journal	Issue	Pages	Year	Title
Vedeneev, V.I., Gol'denberg, M.Ya., and Teitel'boim, M.A.,	<i>Kinet. Catal.</i>	28,	1055-1059	(1987).	<i>Calculation of the rate constant of the reaction CF<sub>3</sub> + O<sub>2</sub> = CF<sub>3</sub>O + O by the transition state method.</i>
Vedeneev, V.I., Teitel'boim, M.A., and Shoikhet, A.A.,	<i>Bull. Acad. Sci. USSR, Div. Chem. Sci.</i>	8,	1534-1537	(1978).	<i>The photolysis of CF<sub>3</sub>I in the presence of O<sub>2</sub> and Br<sub>2</sub>. I. The mechanism of the elementary step in the reaction of CF<sub>3</sub> radicals with O<sub>2</sub>,</i>



## 6.10. Oxidized Fluorocarbon Kinetics

Authors	Journal	Issue	Pages	Year	Title
Batt, L. and Walsh, R.,	<i>Inter. J. Chem. Kin.</i>	14,	933-944	(1982).	<i>A reexamination of the pyrolysis of bis-trifluoromethyl peroxide,</i>
Behr, P., Goldbach, K., and Heydtmann, H.,	<i>Inter. J. Chem. Kin.</i>	25,	957-967	(1993).	<i>The reaction of fluorine atoms with formyl fluoride and the CFO self-reaction at 293K,</i>
Bevilacqua, T.J., Hanson, D.R., Howard, C.J.,	<i>J. Phys. Chem.</i>	97,	3750-3757	(1993).	<i>Chemical ionization mass spectrometric studies of the gas-phase reaction of CF3O<sub>2</sub>+NO, CF3O+NO, and CF3O+RH,</i>
Chen, J., Zhu, T., Niki, H., and Mains, G.J.,	<i>Geophys. Res. Lett.</i>	19,	2215-2218	(1992).	<i>Long path FTIR spectroscopic study of the reactions of CFO radicals with ethane and propane,</i>
Chen, J., Zhu, T., Young, V., Niki, H.,	<i>J. Phys. Chem.</i>	97,	7174-7177	(1993).	<i>Long path FTIR spectroscopic study of the reactions of CFO radicals with alkenes,</i>
Choi, Y.S. and Moore, C.B.,	<i>J. Chem. Phys.</i>	97,	1010-1021	(1992).	<i>State-Specific Unimolecular Reaction Dynamics of HF<sub>CO</sub>. I. Dissociation Rates,</i>
Cobos, C.J.,	<i>An. Asoc. Quim. Argent.</i>	73,	269	(1985).	<i>Theoretical analysis of the unimolecular decompositions CF3OF = CF3O + F, CF3OOCF3 = CF3O + CF3O, and CF3OOOF3 = CF3O + CF3O<sub>2</sub>,</i>
Croce, A.E., Tori, C.A. and Castellano, E.,	<i>Z. Phys. Chem. (Neue Folge)</i>	162,	161	(1989).	<i>Kinetics of CF2O production in the gas phase thermal reaction between F2O and CO inhibited by O<sub>2</sub>,</i>
Czarnowski, Z. and Czarnowski, J.,	<i>J. Chem. Soc. Faraday Trans.</i>	89,	451-455	(1993).	<i>Kinetics and Mechanism of the Thermal Gas-Phase Reaction Between Trifluoromethylhypofluorite, CF3OF, and Trichloroethene,</i>
Dagaut, P., Wallington, T.J., and Kurylo, M.J.,	<i>Inter. J. Chem. Kin.</i>	20,	815-826	(1988).	<i>The UV absorption spectra and kinetics of the self-reactions of CH2ClO<sub>2</sub> and CH<sub>2</sub>FO<sub>2</sub> radicals in the gas phase,</i>
Francisco, J.S. and Goldstein, A.N.,	<i>Chem. Phys.</i>	127,	73-79	(1988).	<i>Dissociation dynamics of FC(O)O and ClC(O)O radicals,</i>
Francisco, J.S. and Mina-Camilde, N.,	<i>Can. J. Chem.</i>	71,	135-140	(1993).	<i>A study of hydrogen abstraction reactions by halogen atoms with HFCO and HCICO - Determination of transition state structures, barrier heights, and vibrational frequencies,</i>
Francisco, J.S. and Zhao, Y.,	<i>Chem. Phys. Lett.</i>	153,	296-302	(1988).	<i>Energetics of the reactions of FCO with O<sub>2</sub> using unrestricted Moller-Plesset perturbation theory with spin annihilation,</i>
Francisco, J.S. and Zhao, Y.,	<i>J. Chem. Phys.</i>	93,	276-286	(1990).	<i>The reaction of atomic fluorine with formyl fluoride: An experimental and theoretical study,</i>
Francisco, J.S. and Zhao, Y.,	<i>Chem. Phys. Lett.</i>	96,	7587-7596	(1992).	<i>Ab initio studies of dissociation pathways on the ground state potential energy surface for HF<sub>CO</sub> and HCICO,</i>
Francisco, J.S.,		163,	375-380	(1989).	<i>Decomposition pathways of carbonfluorochloroic acid on the ground-state potential energy surface and its implication for a design strategy for alternative halocarbons,</i>
Francisco, J.S.,	<i>J. Atmos. Chem.</i>	16,	285-292	(1992).	<i>A study of the gas-phase reaction of carbonyl fluoride with water,</i>
Francisco, J.S.,	<i>J. Chem. Phys.</i>	96,	7597-7602	(1992).	<i>An examination of substituent effects on the reaction of OH radical with HXCO (where X=H,F, and Cl),</i>
Francisco, J.S.,	<i>J. Chem. Soc. Faraday Trans.</i>	88,	3521-3525	(1992).	<i>Decomposition Pathways for Trifluoroacetic Acid, CF<sub>3</sub>C(O)OH,</i>
Francisco, J.S.,	<i>J. Chem. Soc. Faraday Trans.</i>	88,	1943-1941	(1992).	<i>Reaction of OH radical with CH<sub>3</sub>C(O)H and CF<sub>3</sub>C(O)H,</i>

## 6.10. Oxidized Fluorocarbon Kinetics

Authors	Journal	Issue	Pages	Year	Title
Francisco, J.S., Li, Z., and Williams, I.H.,	<i>Chem. Phys. Lett.</i>	140,	531-536	(1987).	<i>Dissociation dynamics of the trifluoromethoxy radical,</i>
Francisco, J.S., Steinfeld, J.I., Williams, I.H.,	<i>NBS Spec. Publ.</i>	716,	250-255	(1986).	<i>Thermochemistry, structure and reactivity of the trifluoromethoxy radical,</i>
Gangloff, H.J., Milks, D., Malone, K.L., Adams, T.N., and Matula, R.A.,	<i>J. Chem. Phys.</i>	63,	4915-4926	(1975).	<i>An experimental and mechanistic study of the reactions of COF<sub>2</sub> with H and with CO,</i>
Goddard, J.D. and Schaefer, H.F., III,	<i>J. Chem. Phys.</i>	93,	4907-4915	(1990).	<i>Formylfluoride photodissociation: Potential energy surface features of singlet HF<sub>CO</sub>,</i>
Henrici, H., Lin, M.C., and Bauer, S.H.,	<i>J. Chem. Phys.</i>	52,	5834-5842	(1979).	<i>Reactions of F<sub>2</sub>O in shock waves. II. Kinetics and mechanisms of F<sub>2</sub>O-</i>
Heras, J.M., Arvia, A.J., Aymonino, P.J., and Schumacher, H.J.,	<i>An. Assoc. Quim. Argent.</i>	50,	120	(1962).	<i>Estudio cinético de la reacción termica entre fluor, monóxido de carbono y oxígeno,</i>
Kamiya, K. and Morokuman, K.,	<i>J. Chem. Phys.</i>	94,	7287-7298	(1991).	<i>Potential energy surface for unimolecular dissociation and rearrangement reactions of the ground electronic state of HF<sub>CO</sub>,</i>
Lange, W., McCrumb, J.L., Wagner, H. Gg., and Walther, C.D.,	<i>Ber. Bunsenges. Phys. Chem.</i>	81,	720-724	(1977).	<i>Reaktionen von Kohlensuboxid, Teil III. Die Reaktion von Fluor-atomen mit Kohlenstoffsuboxid,</i>
Le Bras, G., Foon, R., and Comboureu, J.,	<i>Chem. Phys. Lett.</i>	73,	357-361	(1980).	<i>EPR kinetic study of the reactions of F and Br atoms with H<sub>2</sub>CO,</i>
Maricq, M.M., Szente, J.J., Khitrov, G.A., and Francisco, J.S.,	<i>Chem. Phys. Lett.</i>	199,	71-77	(1992).	<i>FCO: UV spectrum, self-reaction kinetics and chain reaction with F<sub>2</sub>,</i>
Morokuman, K., Katō, S. and Hirao, K.,	<i>J. Chem. Phys.</i>	72,	6800-6802	(1980).	<i>Substitution effect on formaldehyde photochemistry. Potential surface characteristics of HF<sub>CO</sub>,</i>
Morris, E.R. and Thynne, J.C.J.,	<i>Trans. Faraday Soc.</i>	64,	3027-3034	(1968).	<i>Reactions of radicals containing fluorine. Part 4. Reactions of trifluoromethyl radicals with fluoroaldehyde,</i>
Nielsen, O.J., Ellermann, T., Barkiewicz, E., Wallington, T.J., and Hurley, M.D.,	<i>Chem. Phys. Lett.</i>	192,	82-88	(1992).	<i>UV absorption spectra, kinetics and mechanisms of the self-reaction of CHF<sub>2</sub>O<sub>2</sub> radicals in the gas phase at 298 K,</i>
Plumb, I.C. and Ryan, K.R.,	<i>Chem. Phys. Lett.</i>	92,	236-244	(1982).	<i>Kinetics of the reaction of CF<sub>3</sub>O<sub>2</sub> with NO,</i>
Saathoff, H. and Zellner, R.,	<i>Chem. Phys. Lett.</i>	206,	349-354	(1993).	<i>LIF detection of the CF<sub>3</sub>O radical and kinetics of its reaction with CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>,</i>
Saito, K., Kuroda, H., Kakimoto, T., Munehika, H., and Murakami, I.,	<i>Chem. Phys. Lett.</i>	113,	399-402	(1985).	<i>Thermal unimolecular decomposition of formyl fluoride in Ar,</i>
Sehested, J. and Nielsen, O.J.,	<i>Chem. Phys. Lett.</i>	206,	369-375	(1993).	<i>Absolute rate constants for the reaction of CF<sub>3</sub>O<sub>2</sub> and CF<sub>3</sub>O radicals with NO at 295K,</i>
Sehested, J., Ellerman, T., Nielsen, O.J., Wallington, T.J., and Hurley, M.D.,	<i>Inter. J. Chem. Kin.</i>	25,	701-717	(1993).	<i>UV absorption spectrum, and kinetics and mechanism of the self-reaction of CF<sub>3</sub>CF<sub>2</sub>O<sub>2</sub> radicals in the gas phase at 295K,</i>
Wallington, T.J. and Nielsen, O.J.,	<i>Inter. J. Chem. Kin.</i>	23,	785-798	(1991).	<i>UV absorption spectra and kinetics of the self-reaction of CFCl<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> and CF<sub>2</sub>ClCH<sub>2</sub>O<sub>2</sub> radicals in the gas phase at 298 K,</i>
Wallington, T.J., Ball, J.C., Nielsen, O.J., and Barkiewicz, E.,	<i>J. Phys. Chem.</i>	96,	1241-1246	(1999).	<i>Spectroscopic, kinetic, and mechanistic study of CH<sub>2</sub>FO<sub>2</sub> radicals in the gas phase at 298 K,</i>

## 6.10. Oxidized Fluorocarbon Kinetics

Authors	Journal	Issue	Pages	Year	Title
Zachariah, M.R., Tsang, W., Westmoreland, P.R., and Burgess, D.R.F. Jr.,	<i>J. Phys. Chem.</i>	submitted	(1995).	<i>Theoretical prediction of the thermochemistry and kinetics of reactions of CF2O with hydrogen atoms and water,</i>	
Zhang, F., Francisco, J.S., and Steinfeld, J.I.,	<i>J. Phys. Chem.</i>	86,	2402-2406	(1982).	<i>Multiple infrared photon dissociation and kinetics of CF3O radicals,</i>
Zhao, Y. and Francisco, J.S.,	<i>Chem. Phys. Lett.</i>	199,	65-70	(1992).	<i>An examination of the reaction pathways for the recombination of FCO radicals,</i>



## 6.11. Fluorocarbon Kinetics (Other)

Authors	Journal	Issue	Pages	Year	Title
Ahmed, M.G. and Jones, W.E., Amphlett, J.C. and Whittle, E.,	<i>Can. J. Chem.</i>	63,	2127	(1985).	<i>The kinetics of the reactions of atomic hydrogen with halo-ethylenes, Photoysis of halogens in presence of trifluoroacetaldehyde. Some reactions of the trifluorooacetyl radical,</i>
Amphlett, J.C. and Whittle, E., Arthur, N.L. and Bell, T.N.,	<i>Trans. Faraday Soc.</i>	63,	80-90	(1967).	<i>Bromination of fluoroalkanes. Part 4. Kinetics of thermal bromination of fluoroform and pentafluoroethane,</i>
Ashby, E.C., Deshpande, A.K., Doctorovich, F., Atkinson, B.,	<i>J. Org. Chem.</i>	58,	4205-4206	(1993).	<i>Formation of carbenes from halocarbon radicals,</i>
Ashby, E.C., Deshpande, A.K., Doctorovich, F., R.F., Jr., Kerr, J.A., and Troe, J.,	<i>J. Chem. Soc.</i>	2684-2694	(1952).	<i>The mercury-photosensitised reactions of tetrafluoroethylene, Supplement IV. IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry,</i>	
Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, Basco, N. and Hawthorn, F.G.M., Bait, L. and Mowat, S.I.,	<i>J. Phys. Chem. Ref. Data</i>	21,	1125-1568	(1992).	<i>Evaluated kinetic and photochemical data for atmospheric chemistry.</i>
Bailey, D.L., Cobos, C.J., Cox, R.A., Esser, C., Frank, P., Just, Th., Kerr, J.A., Pilling, M.J., Troe, J., Walker, R.W., and Warnatz, J., Benson, S.W. and Bose, A.N.,	<i>Chem. Phys. Lett.</i>	8,	291-293	(1971).	<i>The electronic absorption spectrum of the trifluoromethyl radical, Inter. J. Chem. Kin.</i>
Benson, S.W. and Haugen, G.R., Benson, S.W.,	<i>Inter. J. Chem. Kin.</i>	16,	603-620	(1984).	<i>The addition of methyl radicals to hexafluoroacetone, Can. J. Chem.</i>
Benes, T., Marta, F., and Szilagyi, I., Brown, C.E., Orlando, J.J., Reid, J., and Smith, D.R., Burgess, D.R.F. Jr., Westmoreland, P.R., Tsang, W., and Zachariah, M.R.,	<i>J. Phys. Chem. Ref. Data</i>	21,	411-429	(1992).	<i>Evaluated kinetic data for combustion modeling, J. Chem. Phys.</i>
Benson, S.W. and Haugen, G.R.,	<i>J. Am. Chem. Soc.</i>	39,	3463-3473	(1963).	<i>Structural aspects of the kinetics of four-center reactions in the vapor phase,</i>
Benson, S.W.,	<i>Can. J. Chem.</i>	87,	4036-4044	(1965).	<i>A simple, self-consistent electrostatic model for quantitative prediction of the activation energies of four-center reactions,</i>
Benes, T., Marta, F., and Szilagyi, I., Brown, C.E., Orlando, J.J., Reid, J., and Smith, D.R., Burgess, D.R.F. Jr., Westmoreland, P.R., Tsang, W., and Zachariah, M.R.,	<i>Chem. Phys. Lett.</i>	61,	881	(1983).	<i>Molecular models for recombination and disproportionation of radicals, J. Chem. Soc. Faraday Trans. Trans.</i>
Benes, T., Marta, F., and Szilagyi, I., Brown, C.E., Orlando, J.J., Reid, J., and Smith, D.R., Burgess, D.R.F. Jr., Westmoreland, P.R., Tsang, W., and Zachariah, M.R.,	<i>Chem. Phys. Lett.</i>	68,	867	(1972).	<i>Reactions of CF<sub>3</sub> radicals with benzotrifluoride and the C-H bond strength in C<sub>6</sub>HSCF<sub>3</sub> and C<sub>6</sub>H<sub>6</sub>, Diode laser detection of transient CF<sub>3</sub> radicals formed by CO<sub>2</sub> laser multiphoton induced dissociation of halocarbons,</i>
Burgess, D.R.F. Jr., Westmoreland, P.R., Tsang, W., and Zachariah, M.R.,	<i>in Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays (eds. W.L. Grosshandler, R.G. Gann, and W.M. Pitts), NIST Special Publication 861, 1994, pp. 467-507</i>				<i>Kinetics of fluorine-initiated flames, Key species and important reactions in fluorinated hydrocarbon flame chemistry,</i>
Cadman et al	<i>ACS Symp. Ser.</i>		in press	(1995).	<i>HF elimination from vinyl fluoride</i>
Cadman, P., Day, M., Kirk, A.W., and Trotman-Dickenson, A.F., Cadman, P., Inel, Y., and Trotman-Dickenson,	<i>Chem. Commun.</i>		453	(1970).	
	<i>J. Chem. Soc. A</i>		1356	(1970).	
	<i>J. Chem. Soc. A</i>		1207-1209	(1970).	<i>Disproportionation of trifluoromethyl and isopropyl radicals,</i>

## 6.11. Fluorocarbon Kinetics (Other)

Authors	Journal	Issue	Pages	Year	Title
Casas, F., Kerr, J.A., and Trotman-Dickenson, A.F.,	<i>J. Chem. Soc.,</i>		1141-1148	(1965).	<i>Fluorinated cyclopropanes. Part III. The reactions of methylene with mono-, 1,1-di-, and tri-fluoroethylene,</i>
Chamberlain, G.A. and Whittle, E.,	<i>J. Chem. Soc. Chem. Comm.</i>	8,	396	(1971).	<i>Photolyses of perfluoroacetic anhydride and perfluoropropionic anhydride vapours. New sources of CF3 and C2F5 radicals,</i>
Chamberlain, G.A. and Whittle, E.,	<i>J. Chem. Soc. Faraday Trans. I</i>	68,	88	(1972).	<i>Photochemistry of anhydrides. Part I. Photoysis of perfluoroacetic anhydrides vapour: A new source of CF3 radicals,</i>
da Cruz, F.N., VanDooren, J., Van Tiggelen, P., Dalby, F.W.,	<i>Bull. Soc. Chim. Belg.</i>	97,	1001	(1988).	
Dodd, R.E. and Smith, J.W.,	<i>J. Chem. Phys.</i>	41,	2297-2303	(1964).	<i>Flash photolysis measurement of the kinetics of CF2 reactions,</i>
Edelbuttel-Einhaus, J., Hoyermann, K., Rohde, G., and Wagner, H.G.,	<i>J. Chem. Soc. Ber. Bunsenges. Phys. Chem.</i>	93,	1413-1416	(1989).	<i>An experimental study of the reactions of CF2(X,A) radicals with NO2, N2O, C2H4, C3H6 in the gas phase,</i>
Fagarash, M.B., Moin, F.B., and Ocheret'ko, L.A., Ferguson, K.C and Whittle, E.,	<i>Kinet. Katal.</i>	9,	762-766	(1968).	<i>Effect of H2 and HCl additions on the photolysis of chlorotrifluoromethane,</i>
Ferguson, K.C and Whittle, E.,	<i>J. Chem. Soc. Faraday Trans. I</i>	68,	306	(1972).	<i>Kinetics of the reaction between HBr and C2F5Br,</i>
Ferguson, K.C. and Whittle, E.,	<i>J. Chem. Soc. Faraday Trans. I</i>	68,	295-305	(1972).	<i>Kinetics of the reaction between HBr and CF3Br. Determination of the bond dissociation energy D(CF3-Br),</i>
Gibian, M.J. and Corley, R.C.,	<i>Chem. Rev.</i>	73,	441-464	(1973).	<i>Organic radical-radical reactions. Disproportionation vs. combination,</i>
Giles, R.D. and Whittle, E.,	<i>Trans. Faraday Soc.</i>	61,	1425-1436	(1965).	<i>Photolysis of mixtures of acetone and hexafluoroacetone: combinations reactions of methyl and trifluoromethyl radicals,</i>
Gozzo, F. and Patrick, C.R., Heinemann, P., Hofmann-Sievert, R., and Hoyerman, K.,	<i>Nature</i>	202,	80	(1964).	
Hiatt, R. and Benson, S.W.,	<i>Symp. Int. Combust.</i>	21,	865	(1988).	<i>Direct study of the reactions of vinyl radicals with hydrogen and oxygen atoms,</i>
Ho, W.-P., Barat, R.B., and Bozzelli, J.W.,	<i>Inter. J. Chem. Kin.</i>	4,	479-486	(1972).	<i>Rate constants for radical recombination. III. The trifluoromethyl radical</i>
Hsu, D.S.Y., Umstead, M.E., and Lin, M.C., Iwaoka, T., Kaneko, C., Shigihara, A., and Ichikawa, H., Johnston, T. and Heicklen, J., Jones, W.E. and Ma, J.L.,	<i>Combust. Flame</i>	88,	265-295	(1992).	<i>Thermal reactions of CH2Cl2 in H2/O2 mixtures: implications for chlorine inhibition of CO conversion to CO2,</i>
Kerr, J.A. and Parsonage, M.J.,	<i>ACS Symp. Ser.</i>	66,	128-151	(1978).	<i>Kinetics and mechanisms of reactions of CF, CHF, and CF2 radicals,</i>
	<i>J. Phys. Org. Chem.</i>	6,	195-200	(1993).	<i>Mechanism of syn addition of molecular fluorine to ethylene - An ab initio MO study,</i>
	<i>J. Chem. Phys.</i>	47,	475-477	(1967).	<i>Fate of difluoromethylene,</i>
	<i>Can. J. Chem.</i>	64,	2192	(1986).	<i>An electron spin resonance study of the reactions of hydrogen atoms with halocarbons,</i>
					<i>Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals</i>

## 6.11. Fluorocarbon Kinetics (Other)

Authors	Journal	Issue	Pages	Year	Title
Kerr, J.A. and Parsonage, M.J.,	<i>with Alkenes, Alkynes, and Aromatic Compounds, Butterworths, London, 1972.</i>				
Kerr, J.A. and Parsonage, M.J.,	<i>Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals, Butterworths, London, 1976.</i>				
Kerr, J.A.,	<i>Chem. Rev.</i>	66,	465	(1966).	
Kondratiev, V.N.,	<i>NBS COM-72-10014,</i>			(1974).	<i>Rate Constants of Gas Phase Reactions,</i>
Kotaka, M., Sato, S., and Shimoskoshi, K.,	<i>J. Fluorine Chem.</i>	41,	371-382	(1988).	<i>INDO study of 1,2-fluorine atom migration in 1,1,2-tetrafluoroethyl radical, cation, and anion,</i>
Mallard, W.G., Westley, F., Herron, J.T., Hampson, R.F., and Frizzell, D.H.,	<i>NIST Standard Reference Database</i>	17,		(1993).	<i>NIST Chemical Kinetics Database - Ver. 5.0,</i>
Meilnikovich, S.V. and Moin, F.B.,	<i>Kin. Catal.</i>	29,	257	(1988).	<i>Kinetics and mechanism of reaction of difluorocarbene with tetrafluoroethylene,</i>
Minato, T., Yamabe, S., Fujimoto, H., and Fukui, K.,	<i>Bull. Chem. Soc. Jpn.</i>	51,	34709	(1978).	<i>A molecular orbital calculation of chemically interacting systems. Interaction between two radicals,</i>
Nilsson, W.B. and Pritchard, G.O.,	<i>Inter. J. Chem. Kin.</i>	14,	299-323	(1982).	<i>Disproportionation reactions between CF2H and C2HS radicals in the gas phase,</i>
Norton, F.J.,	<i>Refrig. Eng.</i>	65,	33	(1957).	
Ogawa, T., Carlson, G.A., and Pimentel, G.C.,	<i>J. Phys. Chem.</i>	74,	2090-2095	(1970).	<i>Reaction rate of trifluoromethyl radicals by rapid scan infrared spectroscopy,</i>
Orlando, J.J. and Smith, D.R.,	<i>J. Phys. Chem.</i>	92,	5147	(1988).	<i>Time-resolved tunable diode laser detection of products of the infrared multiphoton dissociation of hexafluoracetone: A line-strength and band-strength measurement for CF3,</i>
Ortiz de Zarate, A., Castano, F., Fernandez, J.A., Martinez, R., Rayo, M.N.S., and Hancock, G.,	<i>Chem. Phys. Lett.</i>	188,	265-269	(1992).	<i>Removal rates of CHF (A1A(0,0,0)) by alkenes,*</i>
Ortiz de Zarate, A., Martinez, R., Rayo, M.N.S., Castano, F., and Hancock, G.,	<i>J. Chem. Soc. Faraday Trans.</i>	88,	535-541	(1992).	<i>Preparation of CHF (X1A) by infrared multiphoton dissociation and reactions with alkenes,</i>
Pickard, J.M. and Rodgers, A.S.,	<i>J. Am. Chem. Soc.</i>	98,	6115-6118	(1976).	<i>Kinetics of the gas phase addition of bromine to 1,1-difluoroethylene. Pi bond dissociation energy of 1,1-difluoroethylene,</i>
Politanskii, S.F. and Shevchuk, U.V., Politanskii, S.F. and Shevchuk, V.U.,	<i>Kinet. Katal.</i>	9,	496	(1968).	
Pritchard, G.O. and Bryant, J.T.,	<i>J. Phys. Chem.</i>	72,	1603-1611	(1968).	<i>The photolysis of 1,3-difluoro and 1,1,3,3-tetrafluoroacetone at low pressure,</i>
Pritchard, G.O. and Follmer, D.W.,	<i>Inter. J. Chem. Kin.</i>	5,	169-171	(1973).	<i>The deuterium isotope effect in disproportionation of CF2D radicals,</i>
Pritchard, G.O. and Thommarson, R.L.,	<i>J. Phys. Chem.</i>	68,	568-571	(1964).	<i>The C-H bond dissociation energies in CF3H, C2F5H, and C3F7H,</i>
Pritchard, G.O., Abbas, S.H., Kennedy, J.M., Paquette, S.J., Hudson, D.B., Meleason, M.A., and Shoemaker, D.D.,	<i>Inter. J. Chem. Kin.</i>	22,	1051-1069	(1990).	<i>Disproportionation reactions between alkyl and fluoroalkyl radicals. V. Perfluoro-n-propyl and ethyl radicals revisited,</i>

## 6.11. Fluorocarbon Kinetics (Other)

Authors	Journal	Issue	Pages	Year	Title
Pritchard, G.O., Abbas, S.H., Piasecki, M.L., and Meleason, M.A.	<i>Inter. J. Chem. Kin.</i>	23,	431-435	(1991).	<i>Disproportionation reactions between alkyl and fluoralkyl radicals.</i>
Pritchard, G.O., Bryant, J.T., and Thommarson, Shoemaker, D.D., Perkins, J.C., and Leupp, S.L.,	<i>J. Phys. Chem.</i>	69,	664-665	(1965).	<i>The reaction of methyl radicals with methyl and methylene fluoride.</i>
Pritchard, G.O., Folmer, D.W., Meleason, M.A., Pritchard, G.O., Kennedy, V.H., Heldorn, G.M., Piasecki, M.L., Johnson, K.A., and Nilsson, W.B., Raff, L.M.,	<i>Inter. J. Chem. Kin.</i>	24,	735-742	(1992).	<i>Disproportionation reactions between alkyl and fluoralkyl radicals.</i>
Richter, H., Vandooren, J., Van Tiggelen, P., Ruzsicska, B.P., Jodhan, A., Choi, H.K.J., Strausz, O.P., and Bell, T.N.,	<i>Bull. Soc. Chim. Belg.</i>	99,	491	(1990).	<i>Chemistry of carbynes: reactions of CF, CCl, and CBr with alkenes, and Plumb, I.C.,</i>
Seeger, C., Rotzoll, G., Lubbert, A., and Schugerl, K., Selamoglu, N., Rossi, M.J., and Golden, D.M., Shortridge, R.G. and Lin, M.C., Skinner, G.B. and Ringrose, G.H., Smail, T. and Rowland, F.S., Smail, T., Miller, G.E., and Rowland, F.S., Soto, M.R. and Page, M.,	<i>Plasma Chem. Plasma Proc.</i>	4,	141	(1984).	<i>Gas-phase reactions of CF3 and CF2 with hydrogen atoms: Their significance in plasma processing.</i>
Tang, Y.-N. and Rowland, F.S., Tang, Y.-N. and Rowland, F.S., Tedder, J.M. and Walton, J.C.,	<i>Inter. J. Chem. Kinet.</i>	14,	457-469	(1982).	<i>Direct detection of CF2 and computer modeling of its appearance in the fluorination of CH2F2.</i>
Tedder, J.M. and Walton, J.C.,	<i>IEEE J. Quantum Electron.</i>	10,	873-879	(1974).	<i>Mechanism of HF laser emissions from flash-initiated CHFC12 and CH2FC1-NO mixtures.</i>
Tedder, J.M. and Walton, J.C.,	<i>J. Chem. Phys.</i>	43,	4129	(1965).	<i>Shock-tube experiments on inhibition of the hydrogen-oxygen reaction.</i>
Tedder, J.M. and Walton, J.C.,	<i>J. Phys. Chem.</i>	74,	1866-1871	(1970).	<i>The insertion reactions of mono- and difluorocarbene with hydrogen halides.</i>
Tedder, J.M. and Walton, J.C.,	<i>J. Phys. Chem.</i>	74,	3464-3471	(1970).	<i>The reactions of energetic fluorine-18 atoms with tetrafluoroethylene.</i>
Tedder, J.M. and Walton, J.C.,	<i>J. Phys. Chem.</i>	94,	3242-3246	(1990).	<i>Features of the potential energy surface for reactions of OH with CH2O.</i>
Tedder, J.M. and Walton, J.C.,	<i>J. Am. Chem. Soc.</i>	88,	626-627	(1966).	<i>The formation of monofluorocarbene by the gas phase decomposition of dihalomethane molecules excited during atomic exchange reactions,</i>
Tedder, J.M. and Walton, J.C.,	<i>J. Am. Chem. Soc.</i>	89,	6420-6427.	(1999).	<i>The reactions of monofluorocarbene with olefins in the gas phase,</i>
Tedder, J.M. and Walton, J.C.,	<i>Acct. Chem. Res.</i>	9,	183-191	(1976).	<i>The kinetics and orientation of free-radical addition to olefins,</i>

## 6.11. Fluorocarbon Kinetics (Other)

Authors	Journal	Issue	Pages	Year	Title
Tedder, J.M. and Walton, J.C.,	ACS Symp. Ser.	66,	107-127	(1978).	Kinetics and mechanism of the addition of fluorine- <i>c</i> containing radicals to olefins,
Teng, L. and Jones, W. E.,	J. Chem. Soc. Faraday Trans. I	68,	1267-1277	(1972).	Kinetics of the reactions of hydrogen atoms with ethylene and vinyl fluoride,
Teng, L. and Jones, W.E.,	J. Chem. Soc. Faraday Trans. I	69,	189-197	(1973).	Kinetics of the reaction of hydrogen atoms with 1,1-difluoroethylene,
Trotman-Dickenson, A.F. and Milne, G.S.	NSRDS-NBS	9,		(1967).	Tables of bimolecular gas reactions,
Tsai, C. and McFadden, D.L.,	J. Phys. Chem.	93,	2471-2474	(1989).	Gas-phase atom-radical kinetics of atomic hydrogen reactions with CF <sub>3</sub> , CF <sub>2</sub> , and CF radicals,
Tschuikow-Roux, E. and Salomon, D.R.,	J. Phys. Chem.	91,	699-702	(1987).	Photobromination of C <sub>2</sub> H <sub>5</sub> Cl in the presence of C <sub>2</sub> H <sub>6</sub> . The heat of formation of the CH <sub>3</sub> CHCl radical and the D <sub>0</sub> (CH <sub>3</sub> CHCl-H) bond dissociation energy,
Tully, F.P.,	Chem. Phys. Lett.	143,	510-514	(1988).	Hydrogen-atom abstraction from alkenes by OH. Ethene and 1-butene,
Tyerman, W.J.R.,	Trans. Faraday Soc.	65,	1188	(1969).	Rate parameters for reactions of ground-state difluorocarbene and determination of the absolute intensity of the A <sub>1</sub> B <sub>1</sub> -X <sub>1</sub> A <sub>1</sub> absorption bands,
Wong, C.K., Cheung, C.Y., Ma, N.L., and Li, W.K.,	J. Chem. Res. S,		32-33	(1993).	An Ab initio Molecular Orbital Study of the Insertions of Difluorocarbene or Fluorocarbene into Ethene,
Wu, E.-C. and Rodgers, A.S.,	J. Phys. Chem.	78,	2315-2317	(1974).	Thermochemistry of gas-phase equilibrium CF <sub>3</sub> CH <sub>3</sub> +12=CF <sub>3</sub> CH <sub>2</sub> I+HI. The carbon-hydrogen bond dissociation energy in 1,1,1-trifluorohane and the heat of formation of the 2,2,2-trifluoroethyl radical,
Wu, E.C. and Rodgers, A.S.,	J. Am. Chem. Soc.	98,	6112	(1976).	Kinetics of the gas phase reaction of pentfluoroethyl iodide with hydrogen iodide. Enthalpy of formation of the pentfluoroethyl radical and ...
Zachariah, M.R., Westmoreland, P.R., Burgess, D.R.F. Jr., Tsang, W., and Melius, C.F.,	ACS Symp. Ser.			in press (1995).	Theoretical prediction of thermochemical and kinetic properties of fluorocarbons,
Zhitnev, Y.N., Zakharchenko, A.V., Mordkovich, N.Y., Nuggev, T.B.H., Tverinova, E.A., and Timofeev, V.V.,	Laser Chem.	11,	71-81	(1991).	The pulsed homogeneous laser pyrolysis: determination of Arrhenius parameters of CHClF <sub>2</sub> destruction based on the model of physical and chemical processes,



## 6.12. Flame Inhibition (Halogens)

Authors	Journal	Issue	Pages	Year	Title
Bajpai, S.N., Baratov, A.N., Vogman, L.P., Makeev, V.I., Poloznov, N.M., and Petrova, L.D.,	<i>J. Fire Flammability</i>	<b>5</b> ,	255-267	(1974).	<i>An investigation of the extinction of diffusion flames by halons, in Inhibition of Chain Gas Reactions, (ed. Ksandopulo, G.I., Vedeneev, V.I.), Alma-Ata, 1971, pp. 160-172</i>
					<i>Influence of halogenated hydrocarbons on selfignition and flame propagation of hydrogen-air mixtures.</i>
Battin-Leclerc, F., Come, G.M., and Baronnet, F.,	<i>Combust. Flame</i>	<b>99</b> ,	644-652	(1994).	<i>The inhibiting effect of CF3Br on the reaction of CH4 + O2 at 1070 K, Flame structure studies of CF3Br-inhibited methane flames. II. Kinetics and mechanisms,</i>
Biordi, J.C., Lazzara, C.P., and Papp, J.F.,	<i>Symp. Int. Combust.</i>	<b>15</b> ,	917-931	(1974).	<i>Flame structure studies of CF3Br-inhibited methane flames. II. Kinetics and mechanisms,</i>
Biordi, J.C., Lazzara, C.P., and Papp, J.F.,	<i>Symp. Int. Combust.</i>	<b>14</b> ,	367-381	(1973).	<i>Flame-structure studies of CF3Br-inhibited methane flames,</i>
Biordi, J.C., Lazzara, C.P., and Papp, J.F.,	<i>J. Phys. Chem.</i>	<b>80</b> ,	1042-1048	(1976).	<i>Mass spectrometric observation of difluorocarbene and its reactions in inhibition,</i>
Biordi, J.C., Lazzara, C.P., and Papp, J.F.,	<i>J. Phys. Chem.</i>	<b>81</b> ,	1139-1145	(1977).	<i>Flame structure studies of CF3Br-inhibited methane flames. 3. The effect of 1% CF3Br on composition, rate constants, and net reaction rates,</i>
Biordi, J.C., Lazzara, C.P., and Papp, J.F.,	<i>J. Phys. Chem.</i>	<b>82</b> ,	125	(1978).	<i>Flame structure studies of bromotrifluoromethane-inhibited methane flames. 4. Reactions of inhibitor species in flames containing initially 1.1% bromotrifluoromethane,</i>
Brown, N.J., Burdon, M.C., Burgoyne, J.A., and Weinberg, F.J.,	<i>ACS Symp. Ser.</i>	<b>16</b> ,	341-375	(1975).	<i>Halogen kinetics pertinent to flame inhibition: a review,</i>
Burgess, D.R.F. Jr., Westmoreland, P.R., Tsang, W., and Zachariah, M.R.,	<i>Symp. Int. Combust.</i>	<b>5</b> ,	647	(1955).	<i>Effect of methyl bromide on combustion of some fuel-air mixtures, in Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays (eds. W.L. Grosshandler, R.G. Gann, and W.M. Pitts), NIST Special Publication 861, 1994, pp. 467-507</i>
Burgess, D.R.F. Jr., Zachariah, M.R., Tsang, W., and Westmoreland, P.R.,	<i>ACS Symp. Ser.</i>		in press	(1995).	<i>Key species and important reactions in fluorinated hydrocarbon flame chemistry,</i>
Craig, E.C., Cullis, C.F., Fish, A., and Ward, R.B., da Cruz, F.N., VanDooren, J., Van Tiggelen, P., Day, M.J. Stamp, V., Thompson, K., and Dixon-Lewis, G., Dixon-Lewis, G.,	<i>Fire Technol.</i>	<b>8</b> ,	131-141	(1972).	<i>Extinction of fires by halogenated compounds - a suggested mechanism,</i>
	<i>Proc. Roy. Soc. London A</i>	<b>276</b>	527-541	(1963).	<i>The influence of bromine compounds on combustion processes,</i>
	<i>Bull. Soc. Chim. Belg.</i>	<b>97</b> ,	1001	(1988).	
	<i>Symp. Int. Combust.</i>	<b>13</b> ,	705-712	(1971).	<i>Inhibition of hydrogen-air and hydrogen-nitrous oxide flames by halogen compounds,</i>
	<i>Combust. Flame</i>	<b>36</b> ,	1-14	(1979).	<i>Mechanism of inhibition of hydrogen-air flames by hydrogen bromide, Aspects of flame inhibition by halogen compounds,</i>
	<i>Symp. Int. Combust.</i>	<b>16</b> ,	1111-1119	(1977).	<i>The burning velocity of methane-air flames inhibited by methyl bromide,</i>
	<i>Combust. Flame</i>		472-478	(1969).	<i>Mechanism of inhibition of hydrogen-air flames by hydrogen bromide, The burning velocity of methane-air flames inhibited by methyl bromide,</i>
Ellis, O.C., Fenimore, C.P. and Jones, G.W.,	<i>Nature</i>	<b>161</b> ,	402-403	(1948).	<i>Extinction of petrol fires by methyl iodide,</i>
	<i>Combust. Flame</i>	<b>7</b> ,	323-329	(1963).	<i>Flame inhibition by methyl bromide,</i>

## 6.12. Flame Inhibition (Halogens)

Authors	Journal	Issue	Pages	Year	Title
Fristrom, R.M. and Van Tiggelen, P.,	Symp. Int. Combust.	17,	773-785	(1979).	An interpretation of the inhibition of C-H-O flames by C-H-X compounds,
Galant, S.,	Combust. Sci. Technol.	34,	111-148	(1983).	Numerical simulation of unsteady laminar flame propagation via the method of lines: further mathematical refinements and results obtained on halogen inhibition,
Gann, R.G.,	ACS Symp. Ser.	16,	318-340	(1975).	Initial reactions in flame inhibition by halogenated hydrocarbons,
Garner, F.H., Long, R., Graham, A.J.,	Symp. Int. Combust.	6,	802-806	(1957).	The effect of certain halogenated methanes on pre-mixed and diffusion flames,
Badakhshan, A.,	J. Res. NBS	70A,	133-141	(1966).	Effect of some halogenated hydrocarbons on the flame speed of methane,
Halpern, C.,	Combust. Flame	59,	93-95	(1985).	Inhibition of the H2-O2 reaction by CF3Cl,
Hidaka, Y., Kawano, H., and Suga, M.	Combust. Flame	60,	233-238	(1985).	Additive effect of CF3Cl on OH, CH, and C2 emissions: shock tube study with C2H4-O2-CF3Cl and CH4-O2-CF3Cl mixtures,
Hidaka, Y. and Suga, M.	Combust. Flame	62,	183-191	(1985).	Effect of bromoethane on the ignition in methane-oxygen-argon mixtures behind reflected shock waves,
Ionomata, T., Moriwaki, T., and Okazaki, S.,	Combust. Flame	62,	183-191	(1985).	The influence of dichloro- and trichloro-ethylene on the limits of inflammability of carbon monoxide-air mixtures,
Jorissen, W.P. and Langen van der Valk, J.H.A.P.,	Rec. Trav. Chim.	44,	810-813	(1925).	On the mechanism of halogen's flame suppressing properties,
Larsen, E.R. and Ludwig, R.B.,	J. Fire Flammability	10,	69-77	(1979).	JFF/Fire Retardant 1, 4-12 (1974). Mechanism of flame inhibition. I: The role of halogens, II: Mechanism of flame inhibition. II: A new principle of flame suppression,
Larsen, E.R.,	JFF/Fire Retardant	2,	5-20	(1975).	Flame inhibition by hydrogen halides: some spectroscopic measurements,
Lerner, N.R. and Cagliostro, D.E.,	Combust. Flame	21,	315-320	(1973).	Structure of laminar nonpremixed flames of methane inhibited with Masri, A.R.,
McHale, E.T., Geary, R.W., von Elbe, G., and Huggett, C.,	Symp. Int. Combust.	24,		(1992).	Structure of laminar nonpremixed flames of methane inhibited with Huggett, C.,
Morris, R.A., Brown, E.R., Viggiano, A.A., Vandoren, J.M., Paulson, J.F., Moteyalli, V.,	Combust. Flame	16,	167-175	(1971).	Flammability limits of H2-O2-fluorocarbon mixtures,
Peeters, J. and Mahnen, G.,	Inter. J. Mass Spectrom. Ion Proc.	121,	95-109	(1992).	Positive Ion Chemistry Related to Hydrocarbon Flames Doped with CF3Br,
Peeters, J. and Mahnen, G.,	Combust. Inst. European Symp., Academic Press, London, I,	1,	53	(1973).	Structure of Ethylene-Oxygen Flames. Reaction Mechanism and Rate Constants of Elementary Reactions,
Pownall, C. and Simmons, R.F.	13th Symp.		585-592	(1971).	The effect of hydrogen bromide on the structure of propane-oxygen flames diluted with argon,
Rae, D. and Thompson, W.	Combust. Flame	35,	131-138	(1979).	Experiments on prevention and suppression of coal-dust explosions by bromochlorodifluoromethane and on prevention by carbon terachloride,
Richter, H., Vandooren, J., Van Tiggelen, P.,	Bull. Soc. Chim. Belg.	99,	491	(1990).	

## 6.12. Flame Inhibition (Halogens)

Authors	Journal	Issue	Pages	Year	Title
Richter, H., Vandooren, J., Van Tiggelen, P.J.,	<i>J. Chim. Phys.</i>	91,	1748-1762	(1994).	Kinetics of the consumption of $CF_3H$ , $CF_2HCl$ , and $CF_2O$ in $H_2O_2$ flames,
Rosser, W.A., Wise, H., and Miller, J.,	<i>Symp. Int. Combust.</i>	7,	175-182	(1958).	Mechanism of combustion inhibition by compounds containing halogens,
Safieh, H.Y., Vandooren, J., and Van Tiggelen, P.J.,	<i>Symp. Int. Combust.</i>	19,	117	(1982).	Experimental Study of Inhibition Induced by $CF_3Br$ in a $CO$ - $H_2$ - $O_2$ - $Ar$ Flame,
Simmons, R.F. and Wright, N.	<i>Combust. Flame</i>	18,	203-206	(1972).	The burning velocities of near limit mixtures of propane, air, and hydrogen bromide,
Simmons, R.F. and Wolfhard, H.G.,	<i>Trans. Faraday Soc.</i>	51,	1211-1217	(1955).	The influence of methyl bromide on flames,
Simmons, R.F. and Wolfhard, H.G.,	<i>Trans. Faraday Soc.</i>	52,	53-59	(1956).	The influence of methyl bromide on flames. Part 2. - Diffusion flames, inhibition of the hydrogen-oxygen reaction by $CF_3Br$ and $CF_2Br$ - $CF_2Br$ ,
Skinner, G.B.,	<i>ACS Symp. Ser.</i>	16,	295-317	(1975).	Bromomethylfluoromethane on the ignition in methane and ethane-oxygen- $T$ ,
Suzuki, A., Inomata, T., Jinno, H., and Moriwaki, T.,	<i>Bull. Chem. Soc. Japan</i>	64,	3345-3354	(1991).	argon mixtures behind shock waves,
Takahashi, K., Inomata, T., Moriwaki, T., and Okazaki, S.	<i>Bull. Chem. Soc. Japan</i>	61,	3307-3313	(1988).	The addition effect of $CH_3Br$ and $CH_3Cl$ on ignition of $CH_4$ by shock waves,
Takahashi, K., Inomata, T., Moriwaki, T., and Okazaki, S.	<i>Bull. Chem. Soc. Japan</i>	62,	636-638	(1989).	The addition effect of $CH_3I$ on the ignition of $CH_4$ by shock waves,
Takahashi, K., Inomata, T., Moriwaki, T., and Okazaki, S.	<i>Bull. Chem. Soc. Japan</i>	62,	2136-2145	(1989).	The addition effects of methyl halides on ethane ignition behind reflected shock waves,
Van Wonterghem, J., Van Tiggelen, A., Vandooren, J.,, da Cruz, F.N., and P. Van Tiggelen,	<i>Bull. Soc. Chim. Belg.</i>	63,	235	(1954).	L'épaisseur et la vitesse de propagation du front de flamme,
Westbrook, C.K.,	<i>Symp. Int. Combust.</i>	22,	1587-1595	(1988).	The Inhibiting Effect of $CF_3H$ on the Structure of a Stoichiometric $H_2/CO/O_2/Ar$ Flame,
Westbrook, C.K.,	<i>Symp. Int. Combust.</i>	19,	127-141	(1982).	Inhibition of hydrocarbon oxidation in laminar flames and detonations by halogenated compounds,
Westbrook, C.K.,	<i>Combust. Sci. Technol.</i>	23,	191-202	(1980).	Inhibition of laminar methane-air and methanol-air flames by hydrogen bromide,
Westbrook, C.K.,	<i>Combust. Sci. Technol.</i>	34,	201-225	(1983).	Numerical Modelling of Flame Inhibition by $CF_3Br$ ,
Wilson, W.E., Jr.,	<i>Symp. Int. Combust.</i>	10,	47-54,	(1965).	Structure, kinetics, and mechanisms of a methane-oxygen flame inhibited with methyl bromide,

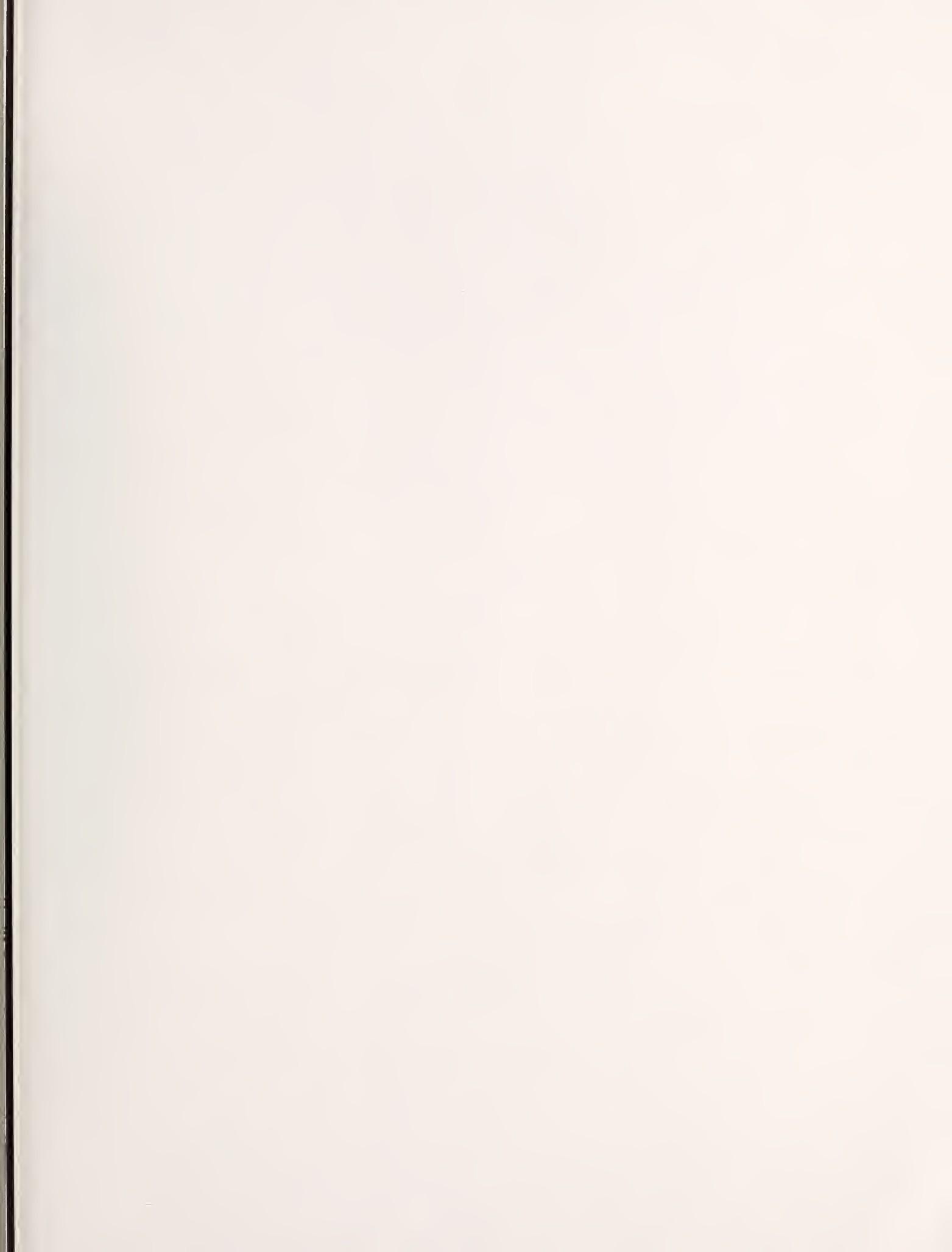


### 6.13. Flame Inhibition (non-Halogens)

Authors	Journal	Issue	Pages	Year	Title
Ashmore, P.G.	<i>Catalysis and Inhibition of Chemical Reactions</i> , London, Butterworths, 1963.				
Birchall, J.D., Blauer, J., Engleman, V.S., and Solomon, W.C., Bregeon, B., Gordon, A.S., and Williams, F.A., Claesson, O., Noda, S., and Yoshida, H., Cohen, A. and Decker, L., Cotton, D.H. and Jenkins, D.R., Creitz, E.C., Friedman, R. and Levy, J.B., Fristrom, R.M., Green, J., Halstead, M.P. and Quinn, C.P., Hastie, J.W., Hastie, J.W., Hertzberg, M., Cashdollar, K.L., Zlochower, I., and Ng, D.L., Homann, K.H. and Poss, R., Ibinicu, M.M. and Gaydon, A.G., Iya, K.S., Wollowitz, S., and Kaskan, W.E., Jensen, D.E. and Jones, G.A., Jones, P.W., Selby, K., Tidball, M.J., and Waddington, D.J., Jonissen, W.P., Jonissen, W.P., Booy, J., and Van Heiningen, J., Jonissen, W.P. and Meuwissen, J.C., Kishore, K. and Mohandas, K.	<i>Combust. Flame</i> <i>Symp. Int. Combust.</i> <i>Combust. Flame</i> <i>Bull. Chem. Soc. Jpn.</i> <i>18th Symp. Trans. Faraday Soc.</i> <i>J. Res. NBS</i> <i>Combust. Flame</i> <i>Fire Res. Abs. Rev.</i> <i>J. Fire Sci.</i> <i>Combust. Flame</i> <i>Combust. Flame</i> <i>J. Res. NBS</i> <i>High Temperature Vapors: Science and Technology</i> , Academic Press, 1975, pp. 332-350	14, 13, 33, 56, 18th Symp. Trans. Faraday Soc. J. Res. NBS Fire Res. Abs. Rev. J. Fire Sci. Combust. Flame Combust. Flame J. Res. NBS High Temperature Vapors: Science and Technology	85-96 109 33-45 2559-2561 225-231 730 521-530 195-201 125-152 470-487 223-230 49-54 733-754 1691-1700 300-302 51-62 415-417 2843-2850 364, 22, 2, 51, 38, 1,	(1970), (1971), (1978), (1983), (1981), (1971), (1970), (1963), (1967), (1992), (1973), (1973), (1973), (1984), (1972), (1964), (1974), (1982), (1978), (1974), (1930), (1932), (1924), (1983).	<i>On the mechanism of flame inhibition by alkali metal salts,</i> <i>Near-limit downward propagation of hydrogen and methane flames in oxygen-nitrogen mixtures, ESR studies of bunsen-type methane-air flames. I. Effects of the entrainment and diffusion of secondary air on the chemical reactions in the flame,</i> <i>Chemical mechanism for secondary flash suppression, Catalysis of radical-recombination reactions in flames by alkali earth metals,</i> <i>Inhibition of opposed-jet methane-air diffusion flames. The effects of alkali metal vapours and organic halides,</i> <i>Combustion Suppression (a literature survey with commentary), A review of phosphorus-containing flame retardants,</i> <i>Inhibition of autoignition at high pressures, Mass spectrometric studies of flame inhibition: analysis of arinonyl trihalides,</i> <i>Molecule basis of flame inhibition,</i> <i>Inhibition and extinction of explosions in heterogeneous mixtures,</i> <i>The effect of pressure on the inhibition of ethylene flames, Spectroscopic studies of the effect of inhibitors on counterflow diffusion flames,</i> <i>The measure of the inhibition of quenched premixed flames,</i> <i>Kinetics of flame inhibition by sodium, Alkaline earth flame chemistry,</i> <i>Inhibition of gas-phase oxidation reactions by aliphatic amines and related compounds,</i> <i>Explosive reactions and negative catalysis, On the prevention of explosive reactions in gas and vapour mixtures by small amounts of various substances,</i> <i>On the influence of some nonflammable vapours of organic liquid on the limits of inflammability of methane air mixtures. II, Does ammonia act as a flame retardant,</i>

### 6.13. Flame Inhibition (non-Halogens)

Authors	Journal	Issue	Pages	Year	Title
Ksandopulo, G.I. and Vedeneev, V.I. (eds.)	Inhibition of Chain Gas Reactions, Alma-Ata, Russian,			1971.	
Kuppu Rao, V. and Prasad, C.R.	Combust. Flame	18,	167-172	(1972).	Knock suppression in petrol engines,
Lask, G. and Wagner, H.G.,	Symp. Int. Combust.	8,	432-438	(1962).	Influence of additives on the velocity of laminar flames,
Libouton, J.C., Dormal, M., and Van Tiggelen,	Symp. Int. Combust.	15,	79-86		
Macek, A.,	AIAA J.	1,	1915-1918	(1963).	Effect of additives on formation of spherical detonation waves in hydrogen-oxygen mixtures,
McHale, E.T.,	Fire Res. Abs. Rev.	11,	90-104	(1969).	Survey of vapor phase chemical agents for combustion suppression,
Milne, T.A., Green, C.L., and Benson, D.K.,	Combust. Flame	15,	255-264	(1970).	The use of the counterflow diffusion flame in studies of inhibition effectiveness,
Mitani, T.,	Combust. Flame	50,	177-188	(1983).	Flame retardant effects of CF <sub>3</sub> Br and NaHCO <sub>3</sub> ,
Moen, I.O., Ward, S.A., Thibault, P.A., Lee, J.H.,					
Krystautas, R., Dean, T., Westbrook, C.K.,	20th Symp.				
Moore, F. and Tipper, C.F.H.,	Combust. Flame	19,	81-87	(1972).	The effect of additives on low-temperature hydrocarbon ignition in a flow system,
Morrison, M.E. and Scheller, K.,	Combust. Flame	18,	34770	(1972).	The effect of burning velocity inhibitors on the ignition of hydrocarbons,
Niioka, T., Mitani, T., Takahashi, M.,	Combust. Flame	50,	89-97	(1983).	Experimental study on inhibited diffusion and premixed flames in a counterflow system,
Noda, S., Fujimoto, S., Claeson, O., and Yoshida, H.,	Bull. Chem. Soc. Jpn.	56,	2562-2564	(1983).	ESR studies of burner-type methane-air flames. II. The effects of the additives,
Petrella, R.V.,	J. Fire Retardant Chem.	6,	125-143	(1979).	The explosive combustion of hydrogen and oxygen inhibited by halogen compounds,
Puri, I.K. and Seshadri, K.,	Combust. Sci. Technol.	53,	55-65	(1987).	The extinction of counterflow premixed flames burning diluted methane-air, and diluted propane-air,
Rosser Jr., W.A., Inami, S.H., and Wise, H.,	Combust. Flame	10,	287-294	(1966).	The quenching of premixed flames by volatile inhibitors,
Seshadri, K.,	Combust. Flame	33,	197-215	(1978).	Structure and extinction of laminar diffusion flames above condensed fuels with water and nitrogen,
Skinner, G.B. and Ringrose, G.H.,	J. Chem. Phys.	42,	2190	(1965).	Ignition delays of a hydrogen-oxygen-argon mixture at relatively low temperatures,
Tipper, C.F.H. and Titchard, A.,	Combust. Flame	16,	223-232	(1971).	The effect of additives on the cool flame combustion of n-heptane,
Williams, F.A.	J. Fire Flammability	5,	54-63	(1974).	A unified view of fire suppression,





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